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Vol. 193 JUNE, 1922 No. 6

THE NATURE OF SPEECH AND ITS INTERPRETATION.*

BY

HARVEY FLETCHER, PH.D.

Research Laboratories of the American Telephone and Telegraph Company and Western Electric Company, Incorporated.

INTRODUCTION.

VARIOUS phases of this subject have received serious study by phoneticians, otologists, and physicists. On account of its universal interest, it has received attention from men in many branches of science. In spite of the large amount of time devoted to the subject, the progress in understanding its fundamental aspects has been rather slow. At the present time the physical properties which differentiate the various fundamental speech sounds are understood in only a very fragmentary way. Some very interesting and pains-taking work has been done on the physical analysis of vowel sounds, but the results to date are far from conclusive. Although several theories have been advanced to explain the way in which the ear interprets sound waves, they are still in the controversial stage.

The material which is presented here is the result of an in investigation which has been carried on in the Research Labora-

*Presented at a meeting of the Electrical Section of The Franklin Institute held Thursday, March 30, 1922.

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tories of the American Telephone and Telegraph Company and Western Electric Company during the past few years.

To make a quantitative study of speech and hearing it is necessary to obtain the speech sounds at varying degrees of loudness and with definitely known amounts of distortion. The main reason why so few real results have been obtained in the investigation of speech sounds is due to the fact that it is extremely difficult to change the volume and distortion of these sounds by acoustic means. Due to recent developments in the electrical transmission of speech it is possible to produce the equivalent of these changes by electrical means. For this purpose a telephone system was constructed which reproduced speech with practically no distortion. It was arranged so that by means of distortionless attenuators the volume of reproduced speech could be varied through a very wide range, and so that by introducing various kinds of electrical apparatus the transmitted speech wave could be distorted in definitely known ways.

A method was developed for measuring quantitatively the ability of the ear to interpret the transmitted speech sounds under different conditions of distortion and loudness. By choosing these conditions properly, considerable information was gained concerning both speech and hearing. This indirect method of attack has a distinct advantage for engineering purposes, in that it measures directly the thing of most interest, namely, the degrading effect upon telephone conversation of introducing electrical distortion into the transmission circuit. However, the application of the results is not limited to this particular field.

METHOD OF MEASURING THE QUALITY OF SPEECH.

Briefly stated the method consists in pronouncing detached speech sounds into the transmitting end of the system and having observers write the sounds which they hear at the receiving end. The comparison of the called sounds with those observed shows the number and kind of errors which are made. The per cent. of the total sounds spoken which are correctly received is called the articulation of the system.

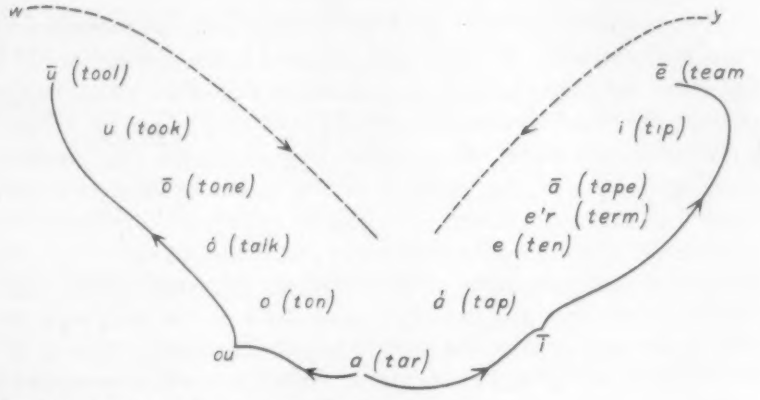
In order to understand the construction of the articulation lists and also to interpret the results of this investigation, I desire to give here a brief classification of the speech sounds, which is based upon the position of the various speech organs when the

sounds are being produced. It is shown in the accompanying table (Table I).

TABLE I.

Classification of the Speech Sounds.

Pure Vowels



Combinational and Transitional Vowels

w – y – ou – ī – h

Semi-vowels

l – r

Stop Consonants

Voiced	Unvoiced	Nasalized	Formation of Stop
b	p	m	lip against lip
d	t	n	tongue against teeth
j	ch	-	tongue against hard palate
g	k	ng	tongue against soft palate

Fricative Consonants

Voiced	Unvoiced	Formation of Air Outlet
v	f	lip to teeth
z	s	teeth to teeth
th (then)	th (thin)	tongue to teeth
zh (azure)	sh	tongue to hard palate

The pure vowels are arranged in the vowel triangle, which is familiar to phoneticians. Starting with the sound ū the lips are rounded and there is formed a single resonant cavity in the front part of the mouth. Passing along the left side of the triangle from ū to a the mouth is gradually opened with the tongue lowered to form the successive vowels. Going along the right side of the

triangle from a to ē, the tongue is gradually raised to the front part of the mouth forming two resonant chambers in the mouth cavity. An infinite number of different shadings of these vowels may be produced by placing the mouth in the various intermediate positions, but the ones which are shown were chosen as being the most distinct.

The sounds w, y, ou, ī and h are classed as combinational and transitional vowels. As the mouth is placed in the position to say ū and then suddenly changed so as to form any other vowel in the triangle, the result obtained is signified in writing by placing the letter w before the vowel. In a similar way we get the effect usually designated by y if the position of the vowel suddenly changes from ē to any other vowel. An infinite variety of dipthongs can be formed by changing the position of the mouth necessary to form one vowel to that to form another without interrupting the voice. The most distinct and principal ones used in our language are formed by passing from the sound a to either extreme corner of the triangle and are known as ou and ī. When a vowel commences a syllable it is formed by suddenly opening the glottis, permitting the air, which has been held in the lungs, to escape into the mouth, which is formed for the proper vowel. If the glottis remains open and the vowel is started by the sudden contraction of the lungs, we have the effect which is represented in writing by placing an h before the vowel. The sounds l and r are called semi-vowels because the voice train is partially interrupted, although the sound can be continued. The stop and fricative consonants are classified in a manner which is familiar to phoneticians.

It will be noticed that the markings are not those used in the international phonetic alphabet which were entirely too complicated for practical use. Only the bar and accent stroke are used. These can be written quickly and with little chance of error.

In order to pronounce these speech sounds properly, they must be combined into syllables. For the purpose of this investigation they were combined into mono-syllables of the simple types consonant-vowel, vowel-consonant, and consonant-vowel-consonant.

To eliminate memory effects every possible combination of the sounds into these types of syllables was used unless there was a good reason for excluding it. The complete list contained 8700 syllables. For convenience of testing these syllables were divided

into groups of fifty. Each group contained the same kind and number of syllable forms and an equal number of each of the fundamental vowel and consonant sounds.

To illustrate the technique of articulation testing a sample list is given in Table II. In the first column the syllable is given in its phonetic form. A key-word showing how each syllable is pronounced is given in the second column. These syllables were written on cards which were shuffled each time before they were used, so that the order in which they were pronounced was entirely haphazard. One hundred and seventy-four similar lists were used in this work. In order to eliminate personal peculiarities, several callers and observers were used. In Table III are shown the results obtained by an observer when this list was transmitted over a system which eliminated all frequencies above 1250 cycles per second.

TABLE II.

Speech-sound Testing List. List No. 160.

	Speech-sound	Key-word		Speech-sound	Key-word
1	ha	ho(t)	26	gōb	go+b
2	hā	hay	27	shōl	shoal
3	wă	wa(g)	28	ros	rus(t)
4	wi	wi(th)	29	jod	ju(g)+d
5	vou	vow	30	bok	buck
6	ăr	air	31	zĭk	z+(d)ike
7	ez	e(bb)+z	32	bĭch	buy+ch
8	ūsh	you+sh	33	kĭth	ki(te)+th
9	an	on	34	gĭt	gui(de)+t
10	id	(l)id	35	yif	y+if
11	jouv	jow(l)+v	36	sin	sin
12	moush	mou(nd)+sh	37	tĕrm	term
13	rour	r+our	38	mĕrl	m+earl
14	zūth	z+(s)oothe	39	pĕrv	p+(n)erve
15	hūs	who+s	40	yēt	y+eat
16	chush	ch+(p)ush	41	bēl	b+eel
17	jum	j+(f)oo(t)+m	42	zef	ze(al)+f
18	thup	th+(s)oo(t)+p	43	weng	whe(n)+ng
19	fuch	foo(t)+ch	44	kev	k+ev(er)
20	wŏng	wa(ll)+ng	45	hăng	hang
21	chŏth	cha(lk)+th	46	păg	p+(r)ag
22	tŏj	ta(ll)+j	47	yās	y+ace
23	kŏg	k+aug(er)	48	dāp	d+ape
24	fōn	(tele)phone	49	yang	ya(cht)+ng
25	dōs	dose	50	lan	l+on

The correct word is written opposite all of the syllables which were recorded incorrectly. The errors for each of the fundamental

sounds were taken from this original sheet and recorded on an analysis sheet as shown on Table IV, for example it will be noticed that p was recorded as k 24.4 per cent., as p 45 per cent., and as t

TABLE III.

TRANSMISSION BRANCH
ARTICULATION TEST RECORDING SHEET

WORD ARTICULATION 40 %

TITLE OF TEST 320311
CONDITION TESTED Low Pass Filter - 1250 ~
Attenuation = 5 napiers down
DATE 2-7-20 OBSERVER M.A.
TEST No. 11 CALLER H. E. D.
LIST No. 1&0

No.	OBSERVED	CALLED	ERRORS	No.	OBSERVED	CALLED	ERRORS
1	tan	te'rm	ā'r-a m-n	26	zip	thup	th-z u-i
2	zit	gît	g-z t-i	27	ko'd	to'j	t-k j-d
3	wa	wa'	a'-a	28	tish	chush	ch-t u-i
4	dāp	✓		29	yang	✓	
5	gāb	✓		30	zāt	zūth	ū-ā th-t
6	yis	yif	f-s	31	ref	ros	e-o e-r
7	māl	mérl	é'r-ā	32	jum	✓	
8	thin	sin	s-th	33	jo'g	ko'g	k-j
9	zīp	zīk	k-p	34	jad	jod	o-a
10	jouv	✓		35	tūth	hūs	h-t s-th
11	yāt	yās	s-t	36	id	✓	
12	thou	vou	v-th	37	ha	✓	
13	bīp	bīch	ch-p	38	fōn	✓	
14	ha'ng	✓		39	ko'th	cho'th	ch-k
15	mīs	moush	ou-ī sh-s	40	rour	✓	
16	dāch	dās	ā-ă s-ch	41	an	✓	
17	kev	✓		42	bok	✓	
18	tig	pa'g	p-t a'-i	43	yāt	✓	
19	kīs	kīth	th-s	44	o'r	a'r	a'-o' g inserted
20	hā	✓		45	yāth	ūsh	ā-ă sh-th
21	weng	✓		46	wa'ng	✓	
22	dāl	bāl	b-d	47	kōv	pérv	p-k ér-ō
23	thich	fuch	f-th u-i	48	zēt	zēf	f-t
24	wif	wi	f inserted	49	lan	✓	
25	ez	✓		50	shāl	✓	

22.2 per cent. of the times called. On the other hand the sound w was only recorded incorrectly 1 per cent. of the times called.

For this system the consonant articulation was 65.8 and the vowel articulation 83.4.

TABLE IV.

Summary Sheet – Average Errors above 5 %

TRANSMISSION BRANCH

ARTICULATION TEST ANALYSIS SHEET

TITLE OF TEST XE0511

CONDITION TESTED Low Pass Filter – 1850~ Attenuation = 5 napiers down Average of

DATE 6-25-20 OBSERVER 3 X

LIST Nos. CALLER 4 E

TEST Nos.

SOUNDS CALLED	SOUNDS RECORDED AS																							Omissions	Insertions	% ERROR
	b	ch	d	f	g	h	j	k	l	m	n	ng	p	r	s	sh	th	t	v	w	y	z				
b			10.2																				4.6			15.2
ch						4.9		6.7							3.2	7.2	4.3	24.7								55.0
d	7.8				11.9		3.3																			23.0
f						3.3									24.6	11.7	19.6						3.9			63.2
g			30.6				3.9																			34.5
h													4.4													13.5
j			15.3		4.0																					29.9
k													3.8					33.7								48.8
l																										2.9
m											2.9															6.8
n									31.7																	35.6
ng																										3.9
p		3.0						24.4										22.8								65.0
r									10.4														5.6			18.6
s				6.2												21.5	24.4	7.9								64.9
sh				3.6											27.3		13.0									53.8
th		2.4		9.6											21.1	8.5			7.0			10.9	2.1			78.7
t		7.3				3.4		18.6					4.8													42.4
v																	10.7					15.1				32.6
w																										1.0
y														9.3												12.8
z			6.5				4.2									6.5	8.9		7.9							29.0

No. of times each sound is called

Total number of sounds called

Total number of errors

Consonant Articulation 65.8

Letter Articulation 72.2

Word Articulation 41.2

Summary Sheet — Average Errors above 2 %

TRANSMISSION BRANCH

ARTICULATION TEST ANALYSIS SHEET

TITLE OF TEST 320X11

CONDITION TESTED Low Pass Filter – 1850~ Attenuation = 5 napiers down Average of

DATE 6-25-20 OBSERVER 3 X

LIST Nos. CALLER 4 E

TEST Nos.

SOUNDS CALLED	No. of Times Called	SOUNDS RECORDED AS														% ERROR
		a	ā	ä	e	ē	ėr	i	ī	o	ō	ó	u	ū	oo	
a	10			10.2												15.1
ā	10															2.2
ä	22	13.8			4.3			2.2				3.8				27.9
e	15		2.4	2.3						10.4						17.6
ē	12															2.9
er	27	3.8	38.8	2.7	4.4					3.6	2.6					60.3
i	11											5.3				8.4
ī	10															4.2
o	11	4.6			24.2											31.9
ō	10															3.9
ó	10	5.4								2.5						10.5
u	10							26.1		4.8						34.6
ū	11											2.9				11.8
oo	10															5.6

Total number of sounds called

Total number of errors

Vowel Articulation 83.4

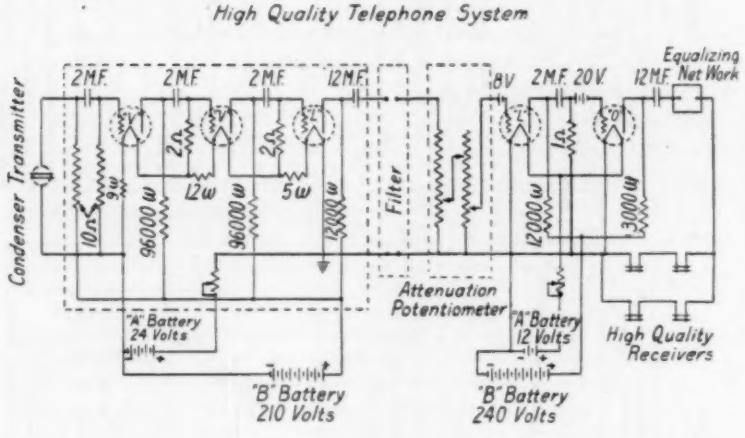
Letter Articulation 72.2

Word Articulation 41.2

DESCRIPTION OF THE SYSTEM FOR REPRODUCING SPEECH SOUNDS.

The telephone system used in this investigation is probably more nearly perfect than any other which has yet been built. Its essential elements are a condenser transmitter to receive the speech waves and transform them into the electrical form, an amplifier for magnifying the intensity of the electrical speech currents, an attenuator for controlling the intensity, an equalizing network, and a receiver for delivering the speech to the ear. A schematic arrangement of the circuit is shown in Fig. 1.

FIG. 1.



A detailed description of the construction and operation of the condenser transmitter has been given by Crandall and Wente and published in the *Physical Review*.[1] It is simply an air condenser, one of its plates being a flexible metal diaphragm.

A five-stage vacuum tube amplifier was used. Particular care was taken in coupling the stages together, so that the amplifier was practically free from frequency distortion.

The attenuator consisted of a potentiometer arrangement which could reduce the amplitude of the speech waves to approximately one-millionth of their maximum values.

The equalizing network was an arrangement of resistances,

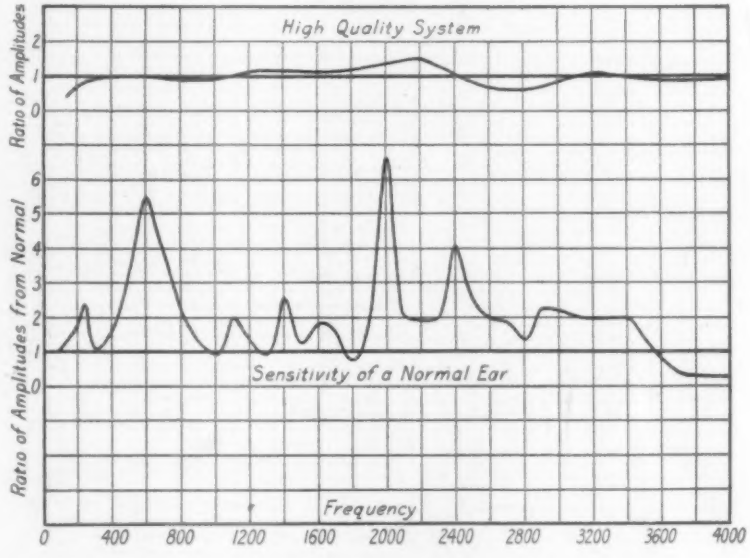
[1] Crandall, *Phys. Rev.*, June, 1918; Wente, *Phys. Rev.*, July, 1917.

condensers and inductance coils having a frequency selectivity which was the complement of that of the rest of the system.

The telephone receiver was a bipolar type having a special construction which was designed to broaden the range of frequency response.

The reproducing efficiency of the system from the mouth of the speaker to the ear of the listener for each frequency is shown in Fig. 2.

FIG. 2.



The pitch or frequency of the tone is given on the X axis. The ordinates represent amplitude ratios or the number of times the amplitude of the tone reaching the ear was greater than that which entered the transmitter. It will be seen that this high quality system has practically a uniform response for all frequencies throughout the speech range.

In order that its uniformity may be appreciated, a comparison curve is given. This curve shows the deviation in the sensitivity of a typical individual ear from the average sensitivity of a large number of ears. The ordinates represent the ratio of amplitudes at the various pitches which was necessary to bring the

tone to the threshold of audibility. It is evident that this deviation is much larger than the departure of the high quality circuit from uniformity.

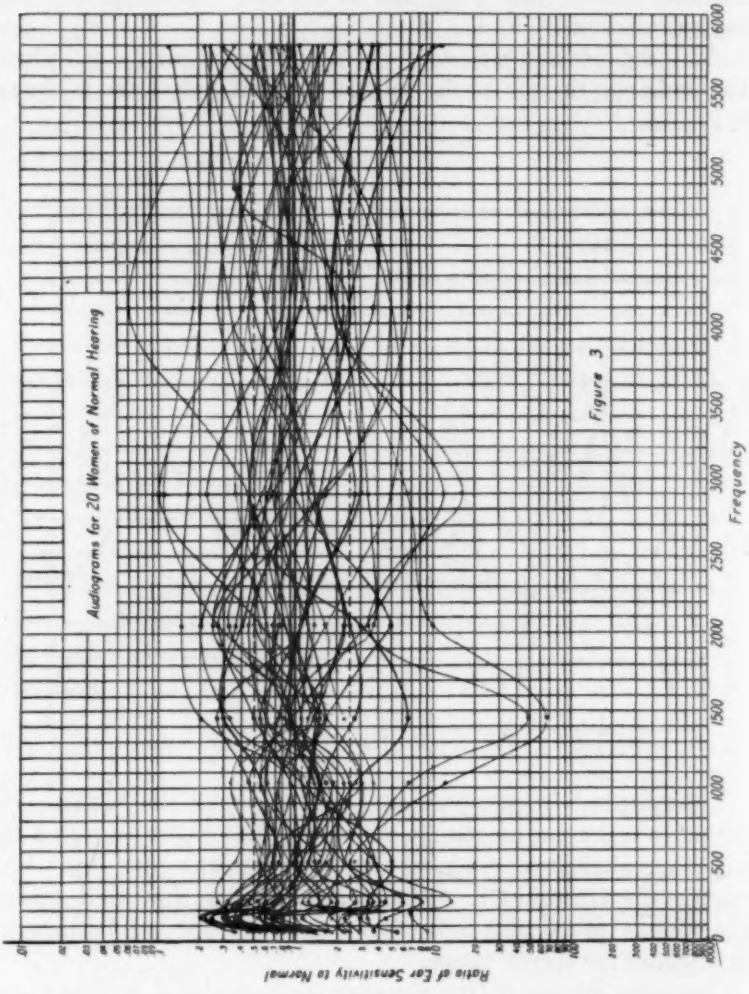


FIG. 3.

To show that this particular individual's curve is typical, the curves for both ears of 20 women are given in Fig. 3. For convenience these curves are plotted on logarithmic paper. If an arithmetic scale is used, all of the curves below the mean are

crowded together in the small space between zero and one, and all those above the mean are stretched out from one to infinity. By using a logarithmic plot a symmetrical distribution is obtained. The method of obtaining these ear sensitivity curves was fully described in a recent paper[2] given before the Natural Academy of Science.

It is interesting to note that they indicate that each individual has a hearing characteristic which is quite different from other individuals. Consequently speech sounds differently to different persons. Any distortions of the speech sounds will necessarily affect some persons differently from others. It is evident then that in discussing speech and hearing we must deal with statistical averages.

Experimental articulation tests showed that the ear interpreted the speech which was transmitted over this high quality system practically as well as that transmitted through the air. Some may wonder why such good quality is not furnished telephone users in commercial practice: Scientifically speaking, it is possible to furnish such quality, but it is evident that the equipment involved is so complicated that such service would be altogether too costly for commercial use; people could not afford to pay for it.

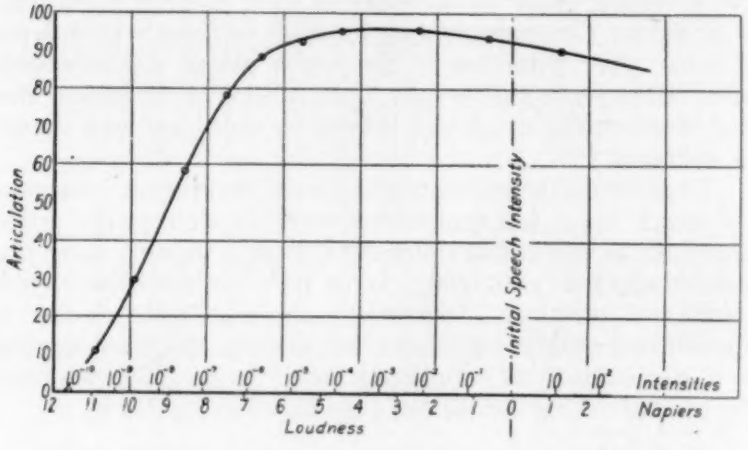
THE RELATION BETWEEN THE VOLUME AND ARTICULATION OF UNDISTORTED SPEECH.

Articulation tests were made upon the high quality telephone system described above when it was set to deliver various intensities from the threshold of audibility to very large values. The results shown as syllable articulation values are given by the curve on Fig. 4. The abscissas in this curve represent loudness and are expressed as the natural logarithm of the number of times the speech wave amplitude has been decreased from the initial intensity at ½ inch in front of the mouth of the callers. This unit of loudness has never been given a name, and as a matter of convenience in this work it is called a napier. It will be noticed that when the volume is reduced 11½ napiers below the initial speech intensity the articulation becomes zero. This point also represents the value at which the speech becomes inaudible and corresponds

[2] Fletcher and Wegel, *Proc. Nat. Acad. Science*, Vol. 8, No. 1, pp. 5-6, Jan., 1922.

to approximately 1/1000 dynes per square centimetre pressure variation against the ear drum. In energy units it is a reduction of ten billion times below the initial speech intensity. For very loud initial speech this point is shifted about 1 napier. For purposes of comparison the intensity reductions are also indicated on the loudness axis.

FIG. 4.



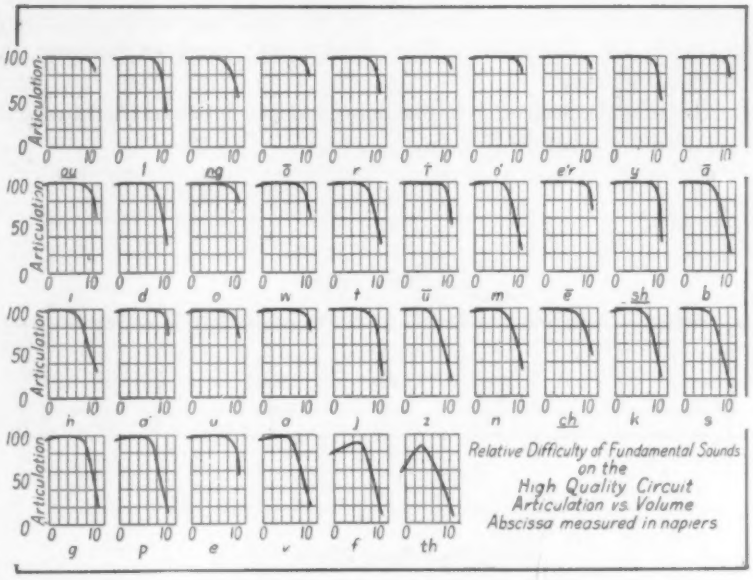
At 3 napiers below or at about 1/1000 of the initial speech intensity the articulation becomes a maximum. Louder speech than this seems to deaden the nerves so that a person makes a less accurate interpretation of the received speech. These results were obtained in a room which was especially constructed to exclude outside noise. When noise is present at the receiving station the optimum loudness increases as the noise increases.

The articulation data were analyzed so as to show the errors of each of the fundamental sounds. The curves given in Fig. 5 show the results of this analysis. It will be noticed that the volume at which errors begin to be appreciable is different for the different sounds and is usually higher for the consonants than for the vowels. Within the precision of the test the intersection point on the X axis was the same for all the sounds, namely at 11.5 napiers.

It will be noticed that the consonants are usually harder to hear than the vowels. However, the speech sounds e and l, r, ng form

notable exceptions to this general rule, since the former is among the most difficult, while the latter are among the very easiest speech sounds. The order in which the speech sounds are given here

FIG. 5.



represents their relative difficulty of interpretation when received at average intensities. At all intensities, the sounds th, f and v are the most difficult. Z, h and s become very difficult at weak volumes. The sounds ṯ, ou, er and ó are missed less than 10 per cent. of the time, even with "very weak" intensity. At "average" volumes there are only three sounds more difficult than e while at "very weak" volumes there are 23 sounds more difficult. At very weak volumes l, which is the easiest sound at "average" volumes is missed three times as often as e.

We will now pass to a consideration of the effect of distortion upon the articulation of the sounds.

DESCRIPTION OF ELECTRICAL FILTERS USED TO PRODUCE DISTORTION.

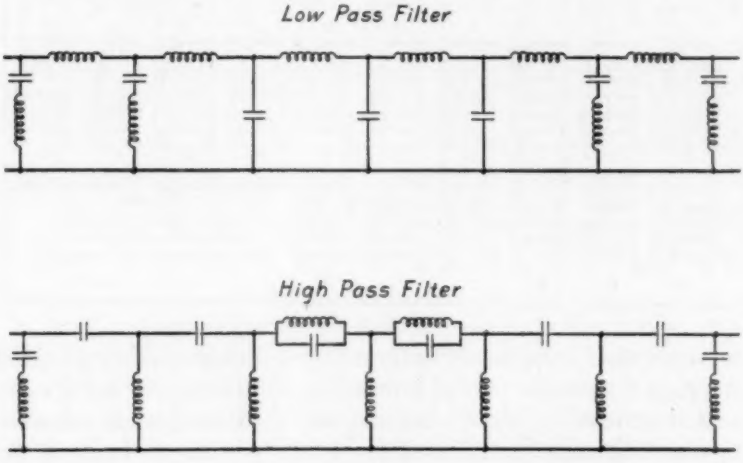
In order to investigate distortion we would like to be able to take the train of speech waves going from the mouth to the ear and operate upon it in various ways such as eliminating frequencies

in certain regions without marring or disturbing other frequencies. For example if all frequencies above 1000 were eliminated it would be possible to determine what intelligibility is carried by this range of frequencies.

Fortunately one of the recent electrical inventions is admirably adapted for this purpose, namely, the electrical wave filter invented by Dr. G. A. Campbell. This device was used extensively in this investigation.

The schematic circuit diagrams of the two types of filters which were used are given in Fig. 6.

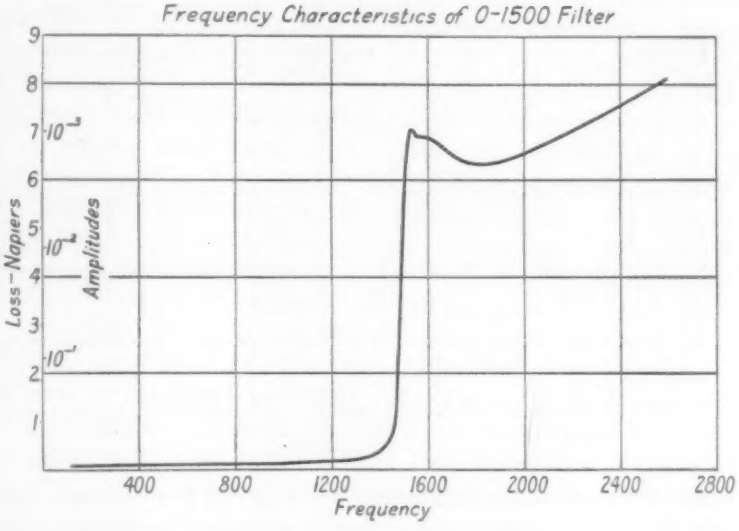
FIG. 6.



This arrangement of coils and condensers produces an electrical conductor with the unusual properties that it transmits without appreciable diminution in amplitude any frequency between certain limits and reduces the amplitude of all frequencies outside these limits to less than 1/1000 of their original value. By varying the numerical values of the inductances and capacities this transmitted range can be placed at any desired position. In the arrangement which was used in the investigation these coils and condensers were housed in two boxes. The switching mechanism was arranged so that by turning a dial the condensers and coils were connected in such a way that the filter transmitted different frequency bands.

In Fig. 7 are shown the transmission properties of the low pass filter when the dial is set to transmit frequencies from 0 to 1500. It is seen that for frequencies below 1400 the amplitudes of the transmitted tones are always greater than .8 of their initial values, while for frequencies above 1500 the amplitudes are decreased to less than .001 of their initial values. These electrical filters were connected into the high quality circuit between the third

FIG. 7.



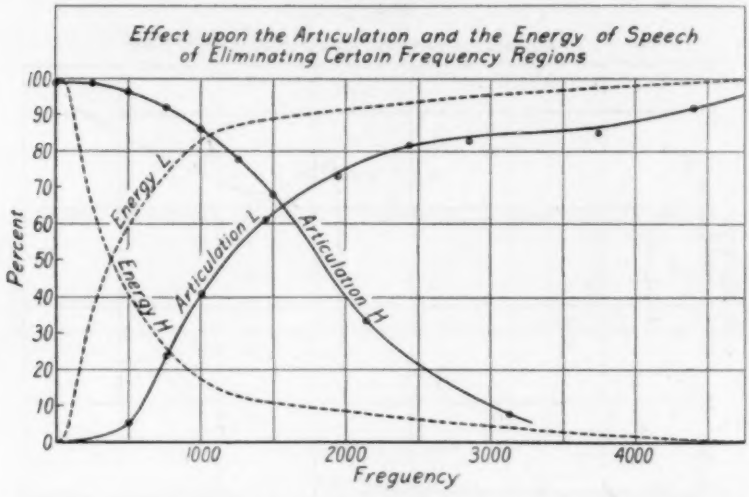
and fourth stages of the amplifier as indicated in Fig. 1. This combination formed a system which would pick up a complex sound wave and transmit faithfully to the ear those component frequencies in any desired region and eliminate all other frequencies.

RESULTS OF ARTICULATION TESTS WITH FILTER SYSTEMS.

Articulation tests were made with these filter systems and the results analyzed as described above. In Fig. 8 the syllable articulation results are shown in graphical form. The ordinates for the solid curves represent the per cent. of the articulation syllables called into the system which were correctly recorded at the observing end. The abscissas represent the so-called " cut off " frequency

of the filter. For example on the curve labelled "Articulation L" the point (1000, 40) means that a system which transmits only frequencies below 1000 cycles per second has a syllable articulation of 40 per cent. Similarly on the curve labelled "Articulation H" the point (1000, 86) means that a system which transmits only frequencies above 1000 cycles per second has a syllable articulation of 86 per cent. The dotted curves show the per cent. of the total

FIG. 8.



speech energy which is transmitted through the filter systems used in the articulation tests. These curves are derived from the results of Crandall and MacKenzie which were recently published.[3]

It will be seen that although the fundamental cord tones with their first few harmonies carry a large portion of the speech energy, they carry practically none of the speech articulation. A filter system which eliminates all frequencies below 500 cycles per second eliminates 60 per cent. of the energy in speech, but only reduces the articulation 2 per cent. A system which eliminates frequencies above 1500 cycles per second eliminates only 10 per cent. of the speech energy, but reduces the articulation 35 per cent. A system which eliminates all frequencies above 3000 cycles per second has as low a value for the articulation as one which eliminates all frequencies below 1000 cycles per second. This last statement may

[3] *Phys. Rev.*, March, 1922.

appear rather astonishing since it is contrary to the popular notion of the relative importance of various voice frequencies from an interpretation standpoint.

The two solid curves intersect on the 1550 cycle abscissa and at 65 per cent. articulation, which shows that using only frequencies above or frequencies below 1550 cycles an articulation of 65 per cent. will be obtained. The two dotted curves necessarily intersect at 50 per cent.

The curves in Fig. 9 show how the articulation of some of the fundamental speech sounds was affected by eliminating certain frequency regions. The ordinate gives the number of times the sound was written correctly per 100 times called. As in Fig. 8 the left hand curve shows the effect of eliminating all frequencies below and the right hand curve the effect of eliminating all frequencies above the frequency specified by the abscissa.

These nine speech sounds were chosen as representing three important classes. It is seen that the long vowels ē, l and ī can be transmitted with an error of less than 3 per cent. when using either half of the range of frequencies. When using either frequencies from 0 to 1700 or from 1700 to infinity ē was interpreted correctly 98 per cent. of the time. Similarly l was interpreted correctly 97 per cent. of the time when using either the range from 0 to 1000 or 1000 to infinity, and ī 96 per cent. of the time when using either the range from 0 to 1350 or from 1350 to infinity. The short vowels, u, o and e are seen to have important characteristics carried by frequencies below 1000. More than a 20 per cent. error is made on any of these three sounds when frequencies below 1000 are eliminated. The elimination of frequencies above 2000 produces almost no effect.

The fricative consonants s, z and th are seen to be affected very differently from those in the other two classes. These sounds are very definitely affected when frequencies above 5000 are eliminated. The sounds s and z are not affected by the elimination frequencies below 1500. It is principally due to these three sounds that the syllable articulation is reduced from 98 per cent. to 82 per cent. when frequencies above 2500 cycles are eliminated.

A more detailed analysis of the articulation results on all the speech sounds showing the kind as well as the number of errors will be given in a future paper.

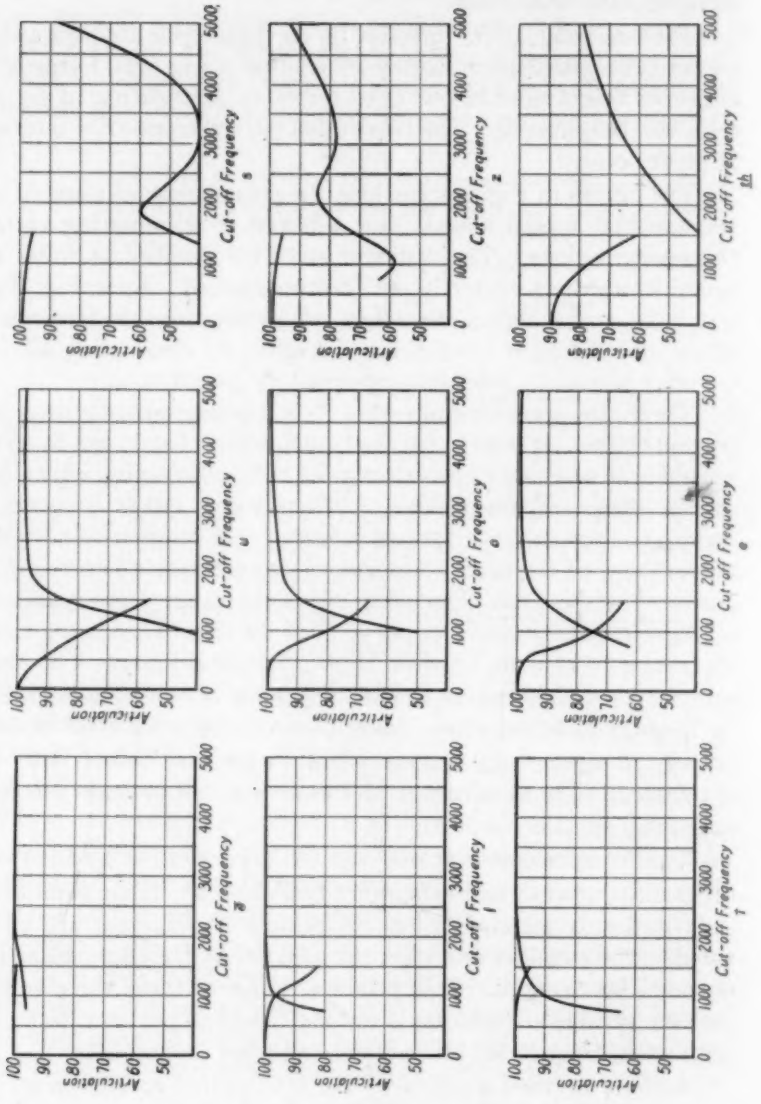

Articulation
Cut-off Frequency
100
90
80
70
60
50
0
1000
2000
3000
4000
5000
s
z
th
u
o
e
ɪ
i
ʌ

FIG. 9.

CONCLUSION.

In conclusion then we see that the intensity of undistorted speech which is received by the ear can be varied from 100 times greater to one-millionth less than the initial speech intensity without noticeably affecting its interpretation. The intensity must be reduced to one-ten-billionth of that initial speech intensity to reach the threshold of audibility for the average ear. Also it is seen that any apparatus designed to reproduce speech and preserve all of its characteristic qualities must transmit frequencies from 100 to above 5000 cycles with approximately the same efficiency. Although most of the energy in speech is carried by frequencies below 1000, the essential characteristics which determine its interpretation are carried mostly by frequencies above 1000 cycles. In ordinary conversation the sounds th, f and v are the most difficult to hear, and are responsible for 50 per cent. of the mistakes of interpretation. The characteristics of these sounds are carried principally by the very high frequencies.

It is evident that progress in the knowledge of speech and hearing has a great human interest. It will greatly aid the linguists, the actors, and the medical specialists. It may lead to improved devices which will alleviate the handicaps of deaf and dumb persons. Furthermore this knowledge will be of great importance to the telephone engineer, and since the telephone is so universally used, any improvement in its quality will be for the public good.

These humanitarian and utilitarian motives as well as the pure scientific interest have already attracted a number of scientists to this field. Now that new and powerful tools are available, it is expected that in the near future more will be led to pursue research along those lines.

LONG-DISTANCE RADIO COMMUNICATION.

BY

L. W. AUSTIN, PH.D., D.Sc.

APRIL, 1922, ISSUE, PAGE 437.

CORRECTION.

Page 445, line two, should read:
at Cavite is 200 amperes and the wave-length 12,100 metres.

An Attempt to Determine Whether a Minimum Time is Necessary to Excite the Human Retina. J. H. J. POOLE. (*Phil. Mag.*, February, 1922.)—The general method employed was this: Light, from a small incandescent lamp passed through a lens, fell upon a plane mirror mounted on top of the vertical shaft of a centrifuge and, after reflection, reached a slit behind which was the eye of the observer. The lens caused the image of the filament to fall upon the slit. When the centrifuge rotated 8000 r.p.m. the eye received light for only a small part of each revolution, but there were many successive flashes in a second. To cut down this number a sectored wheel was interposed between the lamp and the lens. The experiments were conducted in a cellar in order to command large distances and to secure entire darkness.

The adaptation of the eye in the dark is an important factor in the experiments. It takes at least 45 minutes in darkness to attain the greatest sensitiveness, but after 25 minutes the gain is very slow. The eye adapted in the dark is from 5000 to 10,000 times as sensitive as in ordinary daylight.

The duration of the flash received by the eye of the observer could be calculated from the dimensions of the apparatus and the speed of rotation. "It was found that a flash of two ten-millionths seconds was still visible. A flash of duration eight hundred-millionths seconds was, however, found to be invisible. The energy in each of these flashes could be approximately calculated from the candle-power of the radiant and the various dimensions of the apparatus, and it was found that, neglecting any loss by reflexion, etc., the energy in the visible flash was about four ten-millionths erg, while that in the invisible flash was about eight hundred-millionths erg. As to whether the invisibility of the shorter flash is due to its smaller duration alone or simply to the decrease in the energy available, is uncertain. It seems, however, that the latter hypothesis is more probable as the intensity of the longer flash was excessively feeble." G. F. S.

Fertilizer from Wool-scouring Wastes.—F. P. VEITCH (*Jour. Ind. Eng. Chem.*, 1922, xiv, 434) states that, on the average, unscoured wool contains 4 per cent. of water-soluble potash and 0.6 per cent. of water-soluble nitrogen. Both the potash and the nitrogen are present in the wool as water-soluble compounds which are removed by scouring and pass into the sewage from the scouring plant. In this way water courses are polluted, and much valuable fertilizer is lost. In fact, potash worth $840,000 and nitrogenous compounds worth $280,000 as fertilizer are wasted annually. The liquor obtained by scouring may be concentrated and mixed with the wastes from other industries to produce a satisfactory fertilizer.

J. S. H.

PHYSICAL CHEMISTRY AND CERAMICS.*

BY

EDWARD W. WASHBURN, PH.D.

Department of Ceramic Engineering, University of Illinois.

I. INTRODUCTION.

Ceramics.—The term "ceramics" is derived from the Greek "*keramos*" which in turn is related to an older Sanskrit root, meaning "to burn." As used by the Greeks themselves, the primary meaning of "keramos" was simply "burnt stuff," that is, a product obtained by the action of fire, usually upon earthy materials. Modern technical usage in this country is in accord with the original Greek usage, that is, the ceramic industries are those industries which manufacture products by the action of heat on raw materials which are chiefly of an earthy nature. Among these raw materials the element silicon, in the form of its oxide and the compounds thereof (the silicates), occupies a predominant position. In accordance with this definition, the products of ceramic industries include the following:[1]

(1) All kinds of burned clay products, such as stoneware, earthenware, brick, tile, sewer pipe, terra cotta, china, porcelain and so forth.

(2) Cementing materials, such as Portland cement and dental cements; lime, plaster, and a variety of magnesia and gypsum products whose constituents are of an earthy nature and which, after a preliminary treatment which involves a calcination, acquire the property of "setting" to a greater or less extent, when mixed with the proper liquids.

(3) All varieties of glass and glassware including quartz glass, glazes, enamels and many of the artificial precious stones.

(4) Enameled metal products, where the enamel itself is a ceramic material applied to the metal at high temperature, the

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* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute held Thursday, April 6, 1922.

[1] "Rep. of Comm. on Definition," *Jour. Amer. Ceram. Soc.*, 3, 526 (1920).

metal serving only as a skeleton to give the desired form and strength to the glass which it supports.

(5) Refractory articles or materials, either wholly or partially composed of or manufactured from clay, silica (in its various forms), alumina (bauxite), magnesia (magnesite), lime, chromite, asbestos, zirconia, mica, the rare earths, certain carbides and nitrides, and in general any non-metallic product capable of withstanding elevated temperatures. In the case of all products of this class it is evident that a high temperature treatment is fundamental.

(6) Abrasive materials such as carborundum, alundum, and zirconia (and by association, finely divided silica and emery), together with the products manufactured from them by bonding with an earthy material.

(7) Various electrical and thermal insulating products in the manufacture of which earthy materials enter as an important element.

Physical Chemistry.—Physical chemistry is coming to be not so much a definite branch or field of chemistry as it is an attitude or point of view and method of approach to problems in all branches of chemistry. The physical chemists have discovered laws and principles, developed theories and systems of classification, and devised methods and apparatus which have been very successful in enlarging our scientific knowledge of the character and behavior of a great variety of physico-chemical systems. In this way, physico-chemical principles and physico-chemical methods have been successfully employed in the solution of many of the problems of inorganic, organic, physiological, ceramic, mineralogical, geological, sanitary, industrial, analytical, radio and astronomical chemistry.

A discussion of the subject, Physical Chemistry and Ceramics, can therefore be little else than a presentation of examples of ceramic systems in the study of which the methods of the physical chemist have been or might be advantageously employed. I shall, therefore, devote the remaining portion of the discussion to the enumeration and description of instances of this character. Since it is necessary to restrict the scope of the discussion it will be confined to the following five subjects: (1) Colloid chemistry and ceramics; (2) heterogeneous equilibrium at high temperatures; (3) properties of silicate solutions at high temperatures;

(4) high temperature calorimetry; (5) standard methods for testing ceramic materials and products.

II. COLLOID CHEMISTRY AND CERAMICS.

The material to which the term clay is applied is a typical disperse system. Indeed the important properties of plasticity and drying behavior are practically dependent upon the degree of dispersion of the clay material and are to a considerable extent independent of the chemical and mineralogical nature of the particles which make up the clay. From the time the clay is first treated with water in preparation for shaping the body, up to the time when vitrification is well advanced, the clay worker is dealing with a typical colloid.

The phenomenon of plasticity, its magnitude, and the amount of water required to produce its maximum value; the strength of the plastic body, its mobility, its "yield value" and its drying shrinkage are all largely determined by the sizes and size distribution of the individual particles which make up the clay mass. Unfortunately the quantitative relations connecting the above-mentioned properties are at present only slightly and imperfectly known.

The air-dried clay body contains a large quantity of adsorbed water, whose vapor pressure is considerably lower than that of liquid water and which consequently requires higher temperatures for its expulsion. Large quantities of adsorbed permanent gases are also present, both in the raw clay and in the dried body. These gases can be pumped out by heating the clay to about 500° in a suitable vessel connected to a vacuum pump. The resulting dehydrated and out-gassed material possesses pronounced catalytic powers. The amounts and nature of the adsorbed gases have not been systematically studied, nor has the vapor pressure curve of the adsorbed moisture been determined. Both classes of adsorbed materials undoubtedly play an important rôle in the early stages of the firing process and the presence of adsorbed moisture in the right amount is necessary for the shaping of ceramic wares by the dust-press process. There is a large field here for physico-chemical investigation.

The phenomena of deflocculation and flocculation, or peptization and coagulation as they are usually termed by the colloid chemist, are exhibited by all water-clay systems, and are made use

of by the clay worker for purifying his material and in preparing his "slips" for the "casting" process. The physical chemistry of these processes as they take place with clay has received considerable investigation. In general we may say that hydroxyl-ion is a peptizer for clay particles, and definite laboratory methods for determining the proper amounts of water and of peptizer to use in preparing clay slip for a given purpose have been worked out. In some cases the dispersing power of this peptizer is so great that a mass of moist plastic clay can be converted into a comparatively fluid liquid merely by the addition of a small quantity of an alkali.

The phenomenon of cataphoresis is, of course, exhibited by the clay particles in a colloidal suspension and has been studied to some extent with the idea of employing the electric current for the separation and removal of undesirable constituents from the raw clay.

The development of general quantitative laws in the colloid chemistry of clays is rendered difficult by the exceedingly complex nature of the materials dealt with. Only through careful fractionation of the clay, by sedimentation or centrifugation, into portions of definite composition and of uniform particle size, may we hope to obtain systems of sufficiently definite character to make it possible to largely increase our *scientific* knowledge in this field.

In addition to the clay colloids, disperse systems and colloidal processes are met with in ceramics in connection with the preparation and "setting" of cements, limes, and plasters, and in the manufacture of enamels, opalescent glasses, and certain colored glasses such as the gold ruby.

A physico-chemical investigation[2] of the raw material flint, which is a chalcedonic form of silica used in the pottery industry, has shown that it also consists principally of colloidal particles (quartz) and a satisfactory interpretation of its somewhat peculiar behavior on calcination has been obtained as a result of this study. In this investigation the X-ray spectrum apparatus was employed for the final elucidation of the problem. This is probably the first instance in which this new and powerful research tool has been employed in a ceramic investigation. It will in the future undoubtedly be largely used for the study of ceramic materials and products.

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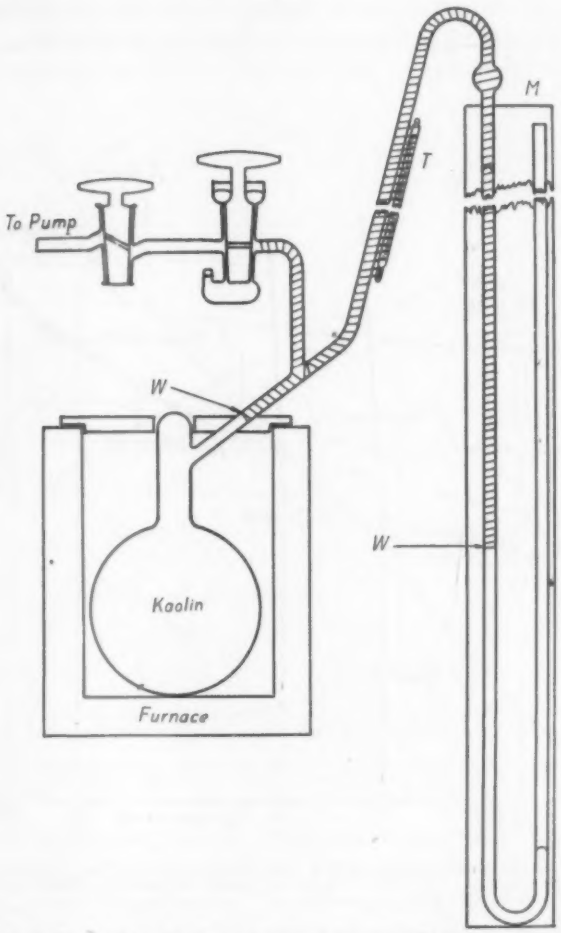
[2] *Proc. Nat. Acad. Sci.*, **8**, 1-5 (1922).

III. HETEROGENEOUS EQUILIBRIUM AT HIGH TEMPERATURES.

The Dissociation of Kaolin.—A considerable amount of the water present in clay is in a chemically combined condition. One

FIG. 1.

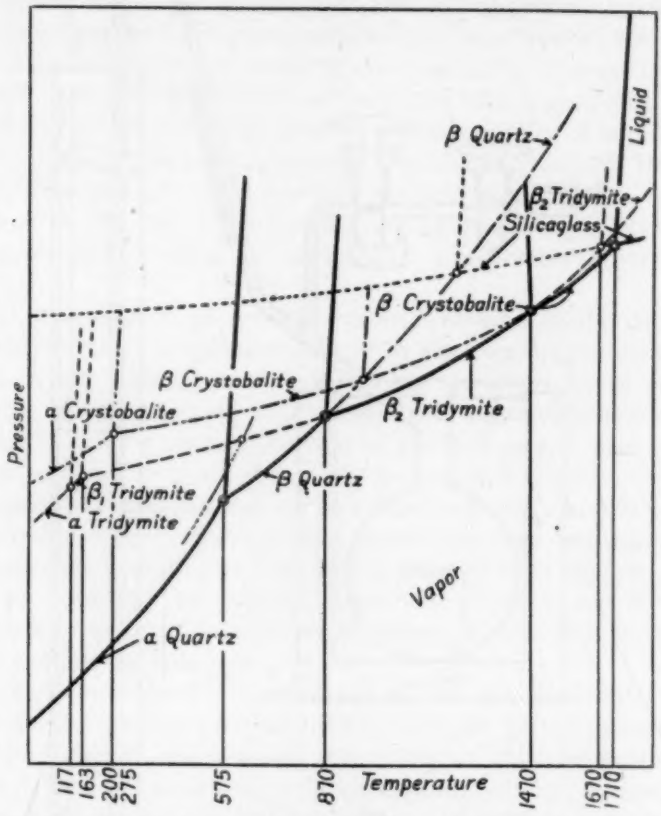


Apparatus for determining the adsorption vapor pressure and the dissociation pressure of kaolin by the static method.

of the most common mineralogical constituents of clay is the substance, kaolin, which, in the purest form in which it is found in nature, is a crystalline mineral (kaolinite) having the chemical composition, $Al_2O_3.2SiO_2.2H_2O$. When a body made of a kaolin

is fired, one of the processes which occurs and completes itself during the early stages of firing is the decomposition of the kaolin molecule with the elimination of the water as vapor. It is not known whether the other constituents of the kaolin molecule

FIG. 2.

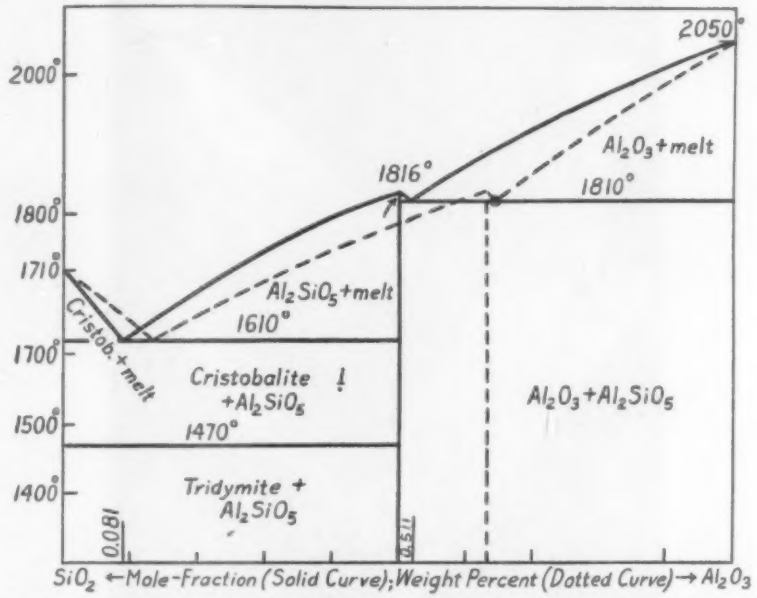


The phase rule diagram for the system SiO_2 showing stable and metastable melting and transition temperatures. The volume changes on passing through the transition temperatures are important and are all known.

remain combined after dehydration or whether they are obtained simply in the form of highly dispersed, possibly amorphous, silica and alumina. A physico-chemical study of the dissociation equilibrium of kaolin at different temperatures would throw much light upon the nature of the process and would, of course, make it possible to calculate thermodynamically the heat of the dehydration

reaction, that is, the amount of heat which must be added to the clay body in order to completely remove the chemically combined water. An investigation of this reaction has been started in the Illinois laboratories, using both the static and the dynamic methods. The principle of the static method is illustrated in Fig. 1. The dynamic method consists simply in passing known quantities of air over an intimate mixture of kaolin with its dehydration products

FIG. 3.



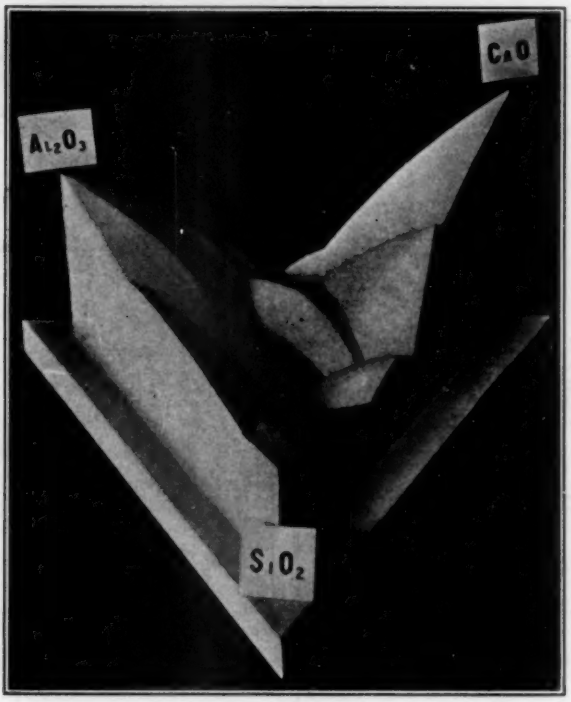
The phase rule diagram for the system SiO_2-Al_2O_3. Dehydrated kaolin belongs to this system. The heat of fusion of SiO_2 can be computed by applying the Solution Laws to this diagram.

kept at a definite temperature, and determining the water content of the air in equilibrium with the mixture.

Phase Rule Diagrams.—The determination of the melting and transition points of any of the earthy oxides used as raw materials in the ceramic industries is not a particularly difficult problem, and most of the melting points are now fairly well known. Since, however, most ceramic bodies are complex systems made up from 2, 3 or more earthy oxides, the phase rule diagrams of the various systems which can be produced with the different oxides are

important, especially for the cement manufacturer, for the manufacturer of bodies which must withstand high temperatures (refractories), as well as for the manufacturer of glass, whose product is a supercooled silicate solution, in which devitrification, that is, crystallization, must be avoided. Most of the phase rule

FIG. 4.



The phase rule diagram for the system SiO_2-Al_2O_3-CaO. Portland cement belongs to this system.

diagrams for ceramic systems which are known at present are the result of the systematic physico-chemical investigations carried out at the Geophysical Laboratory in Washington. Figs. 2, 3, and 4 illustrate the phase rule diagrams of some of the important ceramic systems.

With the aid of these diagrams it is possible to understand and interpret the behavior of ceramic bodies during firing and to

compute for example, the temperatures at which melting will begin and end as well as the amount of the body which can be melted at any given temperature. In the production of a refractory body from any given 2 or 3 oxides as components, the phase rule diagram enables one to tell at once what the possibilities are and

FIG. 5.

Lump of glass before melting.

what the best compositions are as regards resistance to the fluxing action of high temperatures. The more diagrams of this character there are available, and the greater the number of constituents which are covered by the diagrams, the more perfect will become our knowledge of the firing behavior of ceramic bodies and the nature of the attained and attainable completed products.

IV. PROPERTIES OF SILICATE SOLUTIONS AT HIGH TEMPERATURES.

If we carefully cool water, it is possible to cool it considerably below its freezing point before freezing sets in. As the temperature falls the viscosity of the water increases, but never becomes great enough to seriously interfere with that freedom of molecular movement which is necessary in order that the water molecules may arrange themselves into the geometric forms which we call

FIG. 6.

Vacuum furnace. The water-jacketed iron cylinder seats on a rubber gasket on the water-cooled base plate.

crystals. In other words, it has not been possible to supercool water indefinitely without the appearance of the crystalline phase, ice. If, however, we dissolve in the water some material such as sugar, we can prepare a solution or syrup which is very viscous, and on cooling this solution the viscosity increases so rapidly and becomes so great that the molecules of water and of sugar become practically fixed in position and are no longer able to move about with sufficient ease to allow them to group themselves into the geometric forms which we call ice crystals and sugar crystals. In other

words, as the temperature falls, the viscosity continues to increase until finally the syrup becomes hard and brittle, in other words, it is a *glass*, that is, a solid liquid, composed of sugar and water. In the same way the ordinary glass of commerce is a solid supercooled solution of silica and other oxides. A glass differs from a crys-

FIG. 7.

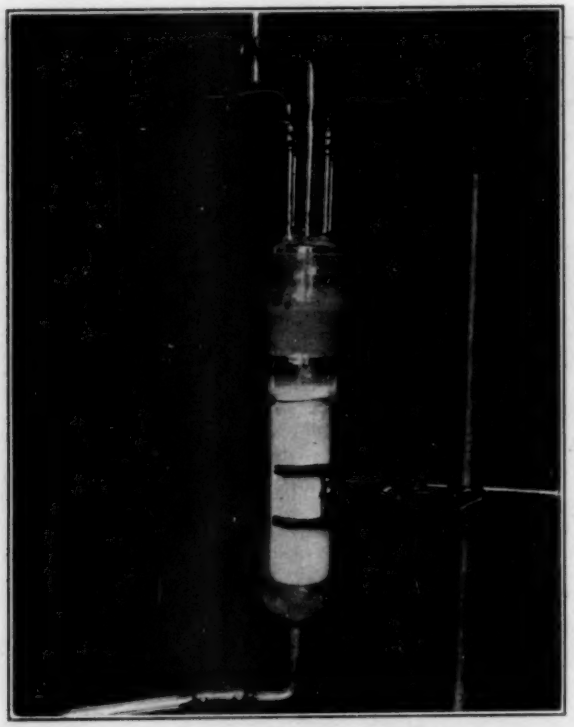
Lump of glass after melting followed by sudden reduction of pressure within the furnace.

talline solid not only in the absence of all crystalline structure, but also in the fact that it has no definite melting point, that is, there is no temperature at which we can say that glass changes from a solid to a fluid. The effect of increased temperature on the glass is simply to gradually soften it, the decrease in the viscosity with increase in temperature being a gradual and continuous process.

Glass is thus a liquid at all temperatures, a very viscous and therefore solid liquid at ordinary temperatures, and a comparatively mobile and fluid liquid at very high temperatures.

The physico-chemical study of aqueous solutions and in general of solutions which are liquid and fluid at ordinary temperatures

FIG. 8.

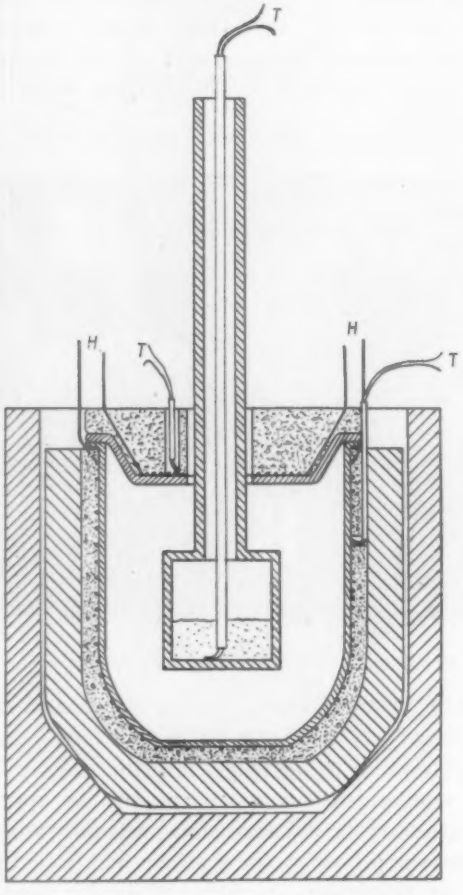


Apparatus for removing, measuring and analyzing the dissolved gases in glass. The glass tube is first evacuated to a high vacuum, the glass in the porcelain crucible is then brought to 1400° and finally allowed to cool to room temperature. The pressure of the evolved gas is measured and by admitting mercury through the inlet at the bottom, the gas is driven out into an Orsat apparatus and analyzed.

has yielded a vast amount of information and has given us numerous laws which have enabled us to systematize our knowledge of the properties and behavior of such solutions. In order to obtain similar knowledge concerning silicate solutions under conditions where the molecules in the solution have freedom of motion, it is necessary to work at elevated temperatures and, except

for the practical difficulties connected with working and making measurements at high temperatures, the methods of attacking the problems of silicate solutions are in no way different from those which have been so successfully employed in the case of aqueous

FIG. 9.

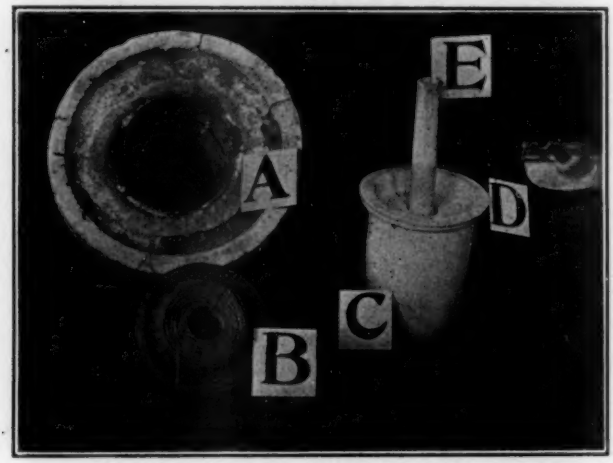


Rotating cylinder apparatus for measuring the viscosity of glass.
H, heating coils; *T*, thermocouples giving identical temperature readings.

solutions at ordinary temperatures. The difficulties associated with accurate physico-chemical measurements at high temperatures are however very real ones, and this is doubtless the reason why so little progress has been made in this field.

We have been attempting at Illinois during the past few years a systematic study of the physical properties of silicate solutions at high temperatures for the purpose of obtaining accurate values of these properties and of correlating, if possible, the data obtained with the composition of the solution. The properties to be investigated naturally include the phase relations (*e.g.*, freezing points and solubilities), density, viscosity, surface tension, electrical conductivity and electrical transference, electrode potentials, diffusion, and vapor pressures. The silicate solutions at high

FIG. 10.



Showing the construction of the heating furnace of the viscosity apparatus.

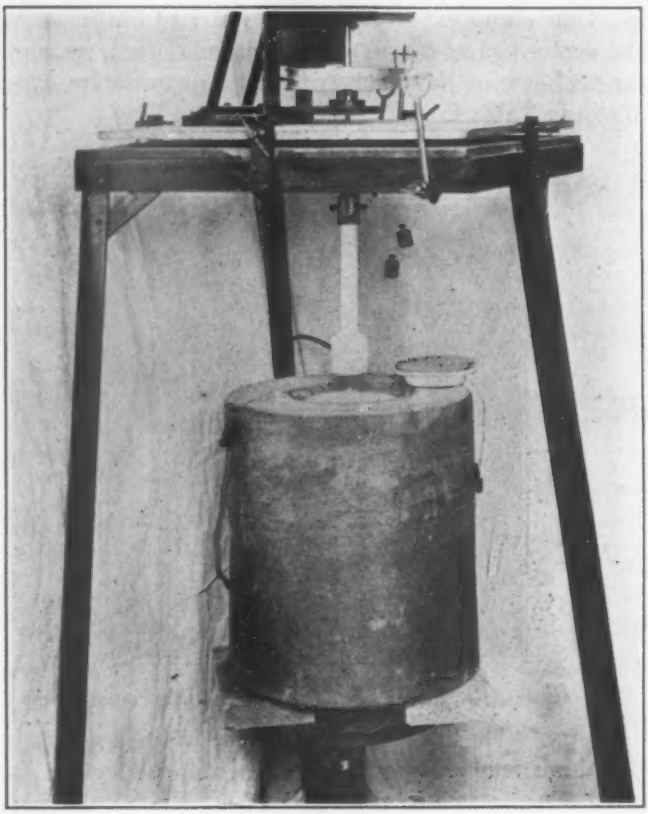
temperatures are typical electrolytic conductors, and in this respect resemble most closely aqueous salt solutions. Some of the difficulties met with in measuring the properties of silicate solutions at high temperatures can perhaps best be appreciated by a brief consideration of the apparatus and methods which have been employed in measuring some of the above-mentioned properties.

Solubility of Gases.—Glass being a liquid, even at ordinary temperatures, should possess the property, characteristic of all liquids, of retaining in solution certain amounts of dissolved gases. The presence of this dissolved gas in ordinary glass can be made apparent by the following experiment:[3]

[3] *Univ. Ill. Eng. Exp. Sta. Bull.*, **18** (1921).

A piece of clear glass free from bubbles, such as that shown in Fig. 5, is placed in a porcelain pot and heated in the closed furnace shown in Fig. 6. When the glass has reached a high temperature

FIG. 11.

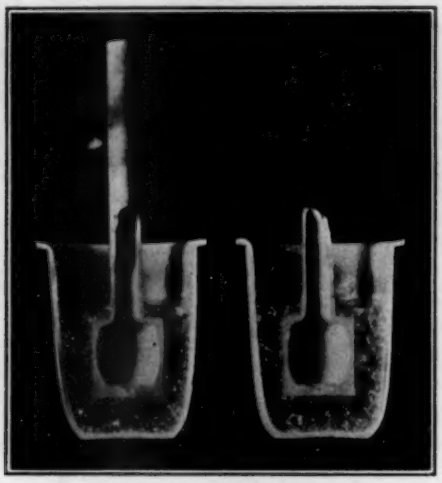


Showing set-up of the viscosity apparatus. After raising the furnace and pot of glass until the stirring cylinder is immersed to the proper depth, the cylinder is rotated by the two falling weights.

and is fairly fluid, the furnace chamber is suddenly connected to the large, previously evacuated tank shown in the figure, thus causing the pressure in the furnace to drop to a low value. Under these circumstances the gases in solution in the glass are immediately evolved, in much the same way as the carbon dioxide comes out of a bottle of soda water when it is opened. The behavior of the glass

is very similar to that of the soda water, it froths and foams vigorously, and after the experiment is over and the glass has cooled down, we discover on opening the furnace that practically all of the glass is found above the pot in the form of a solidified white foam, as shown in Fig. 7. By the use of the apparatus shown in Fig. 8 the above experiment can be carried out in such a way that the evolved gases can be conveniently collected, measured, and analyzed. Some of the results of such a quantitative experiment are shown in Table I.

FIG. 12.

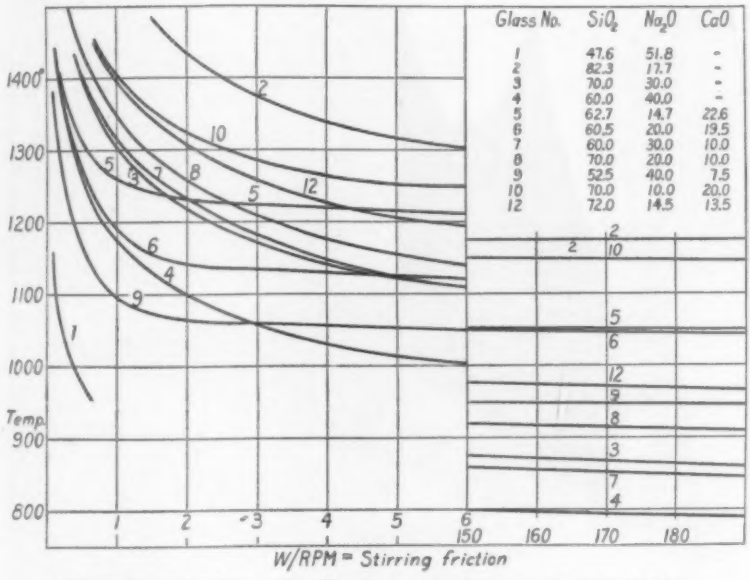


Cross-section of pot and stirring cylinder after completion of an experiment.

Viscosity.—The measurement of the viscosity of a viscous liquid at high temperatures is rendered difficult by the fact that owing to the presence of dissolved gases it is almost impossible to keep the liquid free from bubbles and consequently the customary method of measuring viscosity by the rate of flow of the liquid through a capillary tube is out of the question on account of the great difficulties involved. The presence of these bubbles also makes the adoption of any method depending upon the rate of fall of a sphere through the liquid, undesirable, owing to the fact that bubbles are likely to be picked up during the fall and to produce correspondingly erroneous results. About the only convenient, and at the same time reliable method which can be used for measuring

the viscosity of glass at high temperatures is the method of rotating cylinders which is illustrated by the apparatus shown in Fig. 9. The molten glass is contained in a cylindrical porcelain pot heated on the outside by a platinum heating coil (see Fig. 10). An inner hollow porcelain cylinder with a vertical connecting shaft is coaxial with the outer cylinder and is rotated by any suitable method which enables one to measure the speed of rotation and the power or force required to drive the inner cylinder in the molten

FIG. 13.

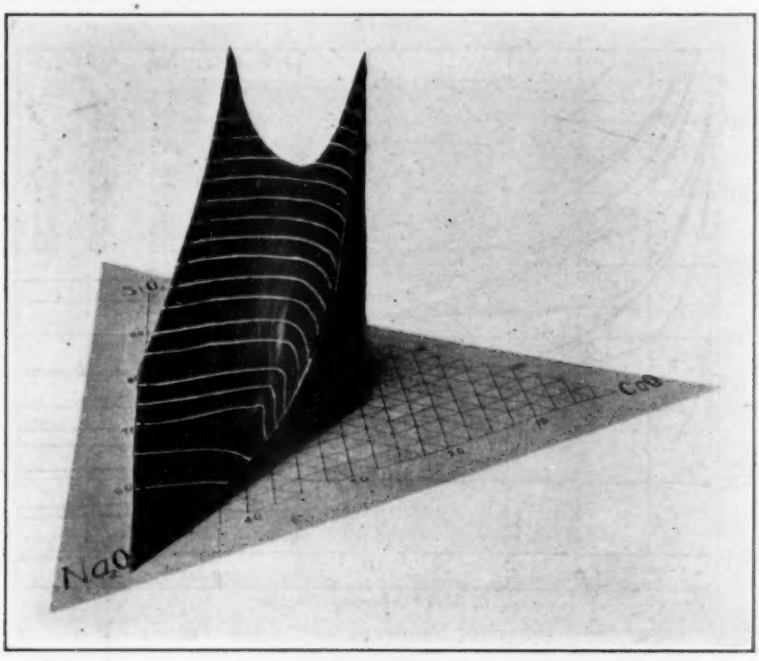


Temperature-viscosity curves. Viscosity expressed in terms of stirring friction.

glass at the speed in question. By determining these two quantities together with the constant of the apparatus, which is obtained by making a similar experiment with a liquid of known viscosity, the viscosity of the glass can be computed. In this way we have investigated at Illinois the complete viscosity-temperature relations for that region of the Na_2O-SiO_2-CaO system within which reasonably stable glasses can be obtained at temperatures below 1500°. The set-up of the apparatus employed in these investigations is shown in Fig. 11, while Fig. 12 shows a cross-section of a pot of glass after the completion of the measurements.

Fig. 13 shows the character of some of the temperature-viscosity curves obtained in this way for glasses of various compositions. By selecting a series of temperatures, and at each temperature reading off from the curves the corresponding viscosities of the various compositions studied, it is possible to prepare a diagram in which compositions are expressed by the usual

FIG. 14.



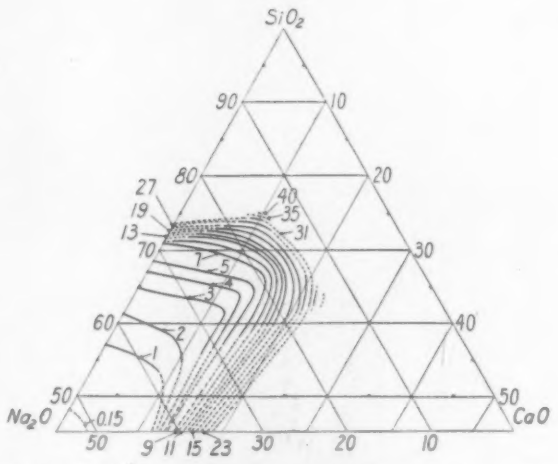
Model showing the viscosity surface at 1400°C.

triangular method and viscosities as the vertical ordinate. Fig. 14 shows a photograph of one of the solid models obtained in this way. The white lines on the model are *isokoms*, that is, lines of constant viscosity. Fig. 15 shows the composition diagram with the projections of the isokoms. From a complete set of diagrams, such as that shown in Fig. 15, one can evidently plot the complete viscosity-temperature curve for a glass of any composition lying within the region studied. In other words, one can read off the viscosity of

any such glass at any temperature within the temperature range employed in commercial glass manufacture.

Surface Tension.—In a manner similar to that employed in connection with the viscosity studies, a systematic study of the surface tensions of the same glasses is also being carried out, and the results will be expressed by diagrams of a similar kind. The apparatus and method employed are illustrated in Fig. 16. A precision of about 0.1 per cent. is obtained on the surface tension measurements. Preliminary results indicate that the surface ten-

FIG. 15.



Isokoms (lines of constant viscosity) at 1400°C. in terms of stirring friction. These isokoms can be translated into poises by means of the standardization curve of the apparatus.

sion of soda-lime-silica glasses between 1200° and 1450° C. is in the order of magnitude of 100 dyne/cm.

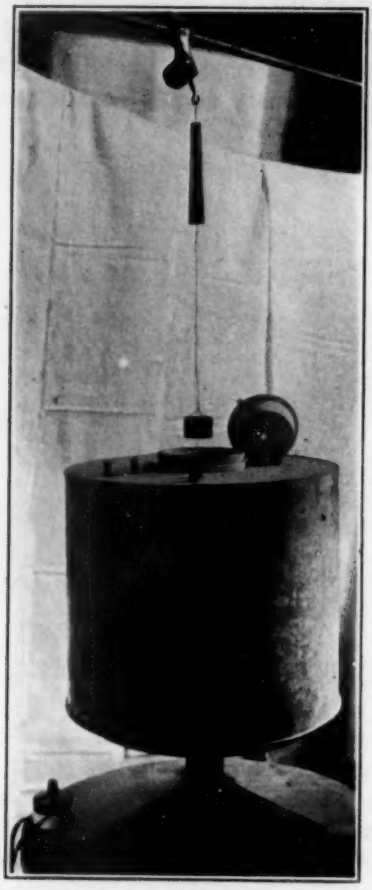
Density.—A similar investigation of the density of the same glasses has been begun, using the principle of Archimedes. The apparatus employed is identical with that used in the surface tension measurements, except that the platinum cylinder is replaced by a small platinum sphere.

Electrical Conductivity.—A systematic investigation of the electrical conductivity of soda-lime-silica glasses has been planned, but no work on this problem has, as yet, been started.

V. HIGH TEMPERATURE CALORIMETRY.

The thermo-chemistry of ceramic systems at high temperatures is practically an unknown field, since no calorimetric methods for determining heat effects of slow reactions at high temperatures

FIG. 16.



Apparatus for measuring the surface tension of molten glass. The coiled spring measures the force with which the platinum cylinder is pulled into the glass surface. When approached from both directions the same equilibrium position is attained. The cylinder is standardized with liquids of known surface tensions.

have been devised. Owing to the lack of such data nothing whatever is known, for example, concerning the amount of heat absorbed by clay bodies during the process of firing. It

has been said with considerable truth that the clay-products manufacturer wastes such a large percentage of the heat which

FIG. 17.

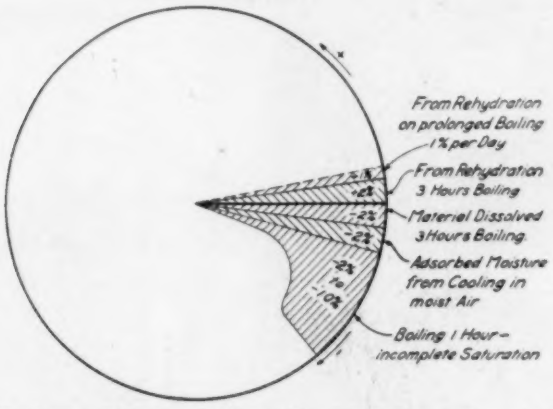
Apparatus for high temperature calorimetry.

he produces for the firing of his kilns, that he is not interested in knowing how much heat his ware must absorb before it is completely burned. While this is perhaps true as regards the total heat absorbed by a ware as fired in the older types of kilns, the kiln of

the future will be a much more efficient furnace, and it will be of interest to ascertain not only the total heat absorbed by the ware during burning, but also the way in which it is absorbed, that is, the amount which must be put into the ware in order to raise its temperature each 100° during firing operation.

In order to be able to measure the heat effects of the chemical and physical processes occurring at high temperatures we have devised at Illinois a calorimeter of the adiabatic type, the parts of which are shown in Fig. 17. The calorimeter consists essentially of an electrically heated alundum furnace tube Q, in which is placed

FIG. 18.

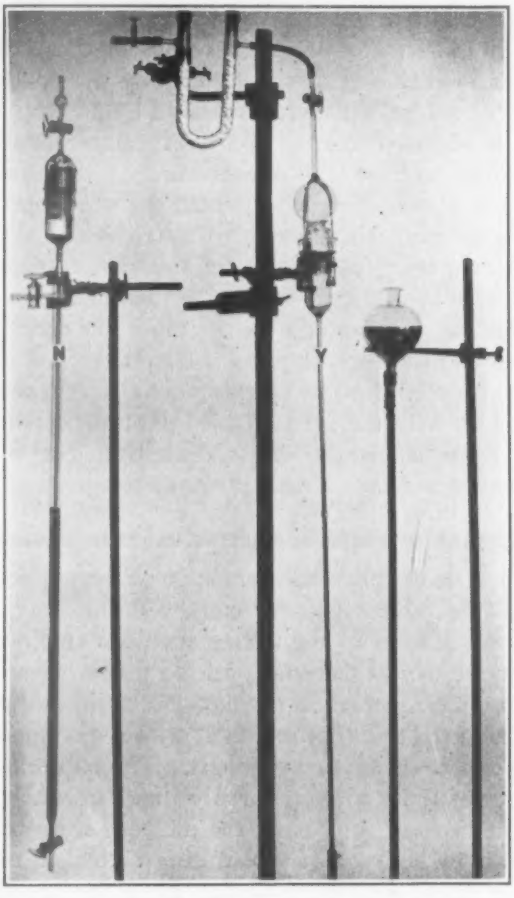

From Rehydration on prolonged Boiling 1% per Day
From Rehydration 3 Hours Boiling
Materiel Dissolved 3 Hours Boiling
Absorbed Moisture from Cooling in moist Air
Boiling 1 Hour — incomplete Saturation

Indicating the nature and magnitudes of some of the sources of error in the "boiling-in-air" method of determining porosity.

the system to be investigated. The platinum heating wire on the furnace tube is protected by a second tube of alundum, J, and by a thin packing of calcined zirconia and finally by one or more glazed refractory tubes, Y, which function as radiation screens. The furnace tube itself, as well as the enclosing tubes, J, Y, are closed at the bottom and furnished with suitable covers at the top. This furnace is suspended within a polished nickel vessel, D, which can be evacuated, and this apparatus is then immersed in the water of the calorimeter, N, in a constant temperature room. The temperature of the water in the calorimeter is always kept the same as that of the room. The leads from the furnace heating coil and the leads for the necessary thermocouples are brought out through air-tight and water-tight connections through the cover, V.

The method of operation consists in passing a metered current of electricity through the heating coil of the furnace until the temperature of the system under investigation has become constant at

FIG. 19.



Washburn-Bunting Porosimeters. N, general laboratory type; accuracy, 0.1 to 0.2 c.c. on pore volume, 0.05 c.c. on bulk volume, rapidity, about 3 minutes per determination. Y, McLeod-gauge type for vitrified porcelains; accuracy 0.01 c.c. on pore volume.

some desired value. At the same time the high speed vacuum pump is kept constantly in operation maintaining a vacuum within the nickel vessel. During the attainment of constant temperature within the furnace, a certain amount of the measured energy input

leaks out into the nickel vessel and is absorbed by the water of the calorimeter, thus tending to raise its temperature. In order to keep the temperature of the calorimeter constant, ice water at 0° is admitted through a valve, 6, the water in the calorimeter being thoroughly stirred meanwhile, and overflowing through a constant level outlet tube into a collecting vessel, 4. As soon as the temperature of the interior of the furnace has become constant, the electric meter is read and at the same time the collector under the overflow of the calorimeter is replaced by an empty one, and the rheostat is adjusted so as to give a larger current through the heating coil and to raise the temperature of the system under investigation to a new level, after which the same operations are repeated. By weighing the amounts of water which overflow from the calorimeter during each stage in the temperature rise, the amount of energy which leaks out of the furnace can be computed and by subtracting this from the energy input, the energy absorbed by the system and the furnace parts is obtained. The constant of the apparatus is determined by carrying out a second similar series of measurements with the furnace filled with a substance, such as quartz for example, whose heat absorption curve has been accurately determined over a wide range of temperature.

VI. STANDARD METHODS OF TESTING CERAMIC MATERIALS.

The services of the physical chemist or of the physicist and the chemist could be advantageously employed for the purpose of making accurate studies of the testing methods employed or proposed for any industrial material. In too many cases the testing methods in use have grown up more or less accidentally and have never been subjected to a thorough and critical examination at the hands of an expert chemist or physicist. The nature and magnitudes of many of the errors present are thus frequently unknown and the possibilities of improving the method, either in accuracy or convenience, or both, or of substituting perhaps a much better method of an entirely different nature, are therefore imperfectly known. The subject of physical chemistry has been built upon a foundation of accurate and careful quantitative measurements of great variety and the physical chemist therefore has the training and knowledge necessary to intelligently criticize testing methods which, after all, are always methods of measurement of some kind.

In order to illustrate the value of a scientific study of testing

methods we undertook at Illinois a critical examination of the methods employed for determining the porosity of ceramic bodies.[4] Porosity is customarily measured by filling the pores of the body, more or less completely, with some liquid and weighing the amount of liquid thus introduced. In order to ascertain the factors which control the rate at which a liquid penetrates small pores, it was found necessary to first develop the laws governing the dynamics of capillary flow. An investigation of the literature apparently showed that this subject had never received any attention, although the statics of capillarity has been, of course, very fully investigated. The laws which were thus derived [5] consisted of quantitative relations connecting the degree of penetrance of a porous body of a liquid, with the time of soaking, the size and length of the capillaries and the surface tension and viscosity of the liquid. The theory indicated that for bodies with very small pores, complete filling of the pores by any liquid could not be effected in any reasonable time without the aid of high vacuum and high pressure equipment. This conclusion was confirmed by experiment. With clay bodies certain other sources of error were also discovered and studied. The nature of some of these is indicated in Fig. 18.

A new method, in which a gas instead of a liquid is employed as the pore filling agent, was finally developed together with a suitable apparatus (Fig. 19) and by means of this method and apparatus it is now possible to carry out porosity determinations far more rapidly, conveniently and accurately than was possible by the method of liquid absorption. The results of this study illustrate some of the possibilities of improving testing methods which may come from a treatment of the method itself as a physico-chemical problem.

On a New Optical Property of Biaxial Crystals. C. V. RAMAN and V. S. TAMMA, India. (*Phil. Mag.*, March, 1922.)—It may be true that "Scientia non scit patriam," but it remains an observed fact that a certain flavor of the soil clings to the work in physics done in each land. The growing school of Indian physicists have taught us to expect in their papers either a different point of view or some subject of investigation that lies apart from those in the prevailing fashion.

[4] *Jour. Amer. Ceram. Soc.*, **4**, 916, 961, 983 (1921); **5**, 48, 112 (1922).

[5] *Phys. Rev.*, **17**, 273 (1921).

"The incandescent filament of a tiny 2-volt lamp or an illuminated pin-hole serves as a suitable source of light. At some distance from it is placed a crystal of aragonite cut and polished with parallel faces at right angles to the bisectrix of the acute angle between the optic axes. On suitably orienting the crystal and examining the pencil of light that has passed through it, a real, erect, unpolarized image of the luminous filament may be easily picked up and traced continuously away from the crystal for a considerable distance. The image is sharp and bright and practically achromatic if the object and the place of observation are both within a few centimetres of the crystal, one on each side.

"It should be remarked that these optical images formed by an aragonite plate differ from those formed by an ordinary converging lens in several respects. The images in the present case are real, erect, and of unit magnification irrespective of the distance of either object or image from the crystal. Further, the image is continuous, that is, it may be observed anywhere in the prolongation of a certain line for a considerable distance from the crystal and not merely at a single point as in the case of images formed by a lens. Also the images appear sharply defined in a field of diffuse light, showing that only part of the energy passing through the crystal is brought to a focus. The object being fixed, the image moves when the orientation of the crystal is altered, but not when the plate is moved in its own plane. The focussing property, in other words, appears to be related to a fixed direction within the crystal. In order that the image may be within the field of observation it is necessary, in fact, that the bundle of light-rays should pass through the crystal roughly in this fixed direction, which appears to be that of either axis of single ray velocity in the crystal." G. F. S.

The Motion of Electrons in Argon. J. S. TOWNSEND and V. A. BAILEY. (*Phil. Mag.*, March, 1922.)—A few months ago these Oxford workers published an account of the motion of electrons in oxygen, nitrogen and hydrogen, and showed how to calculate the mean free path of the electron and its loss of energy upon colliding with a molecule. The same methods are now applied to argon and rather surprising conclusions are reached. "Thus when an electron moving with a velocity of the order of 10^8 centimetres per second collides with a molecule of argon it loses about one ten-thousandth part of its energy, but when it collides with molecules of the other gases it loses more than 1 per cent. of its energy. Also the mean free path of an electron moving with these velocities in argon is about ten times as long as its mean free path in the other gases at the same pressure." Whatever in argon may cause the long free path, it cannot be the small diameter of its molecule, for they are smaller than those of nitrogen and larger than those of hydrogen.

G. F. S.

RECENT ADVANCES IN APPLIED ELECTROCHEMISTRY.*

BY

MAURICE DE KAY THOMPSON, Ph.D.

Department of Physics, Massachusetts Institute of Technology.

APPLIED electrochemistry consists of the following rather diverse subjects:

(1) Electroplating and galvanoplastic processes, such as electrotyping; (2) wet electrometallurgy; (3) the electrolytic production of chemical compounds in aqueous solutions; (4) primary and secondary cells; (5) electric furnace products, and the furnaces in which they are made; and (6) gas reactions produced by electricity.

It may be well, first, to explain what will be considered advances in this applied science. There may be differences of opinion on this point, but it will here be considered that an increase in the quantity or improvement of the quality of an electrochemical product, an improvement in method, apparatus, or efficiency of production, or the extension of electrochemical methods to new products, would all be advances.

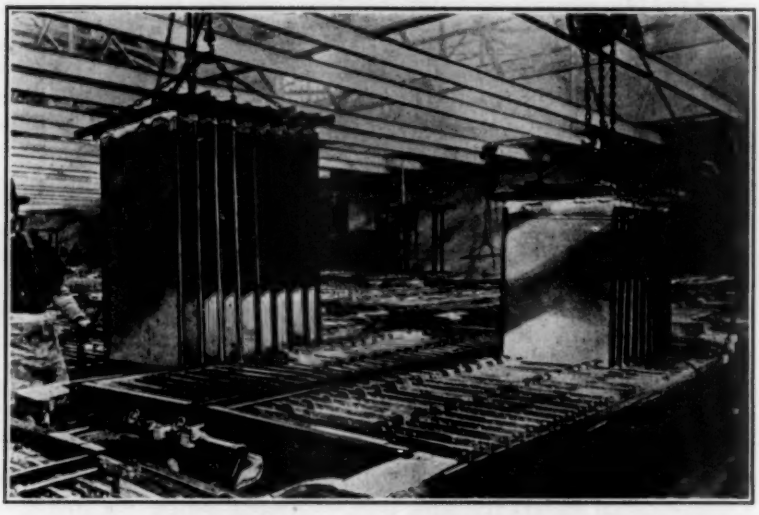
Electroplating and electrotyping are the earliest industrial application of electricity, and were practiced before the invention of the dynamo machine. Originally electroplating was confined largely to the deposition of gold and silver for decorative purposes, but it has developed more and more into use as a means of depositing protective coatings. If it is also pleasing of appearance, so much the better, as in the case of nickel plating, which was first developed in this country. A recent improvement in nickel plating consists in the use of nickel fluoride in place of nickel chloride or sulfate, because the fluoride gives a finer grained deposit with higher tensile strength and greater hardness.[1] This is another example of the familiar fact that the quality of the deposit of metals depends to a large extent on the salt from which it is deposited.

* Presented at the Stated Meeting of the Institute held Wednesday, March 15, 1922.

[1] Blum, *Tr. Am. Electroch. Soc.* for 1921.

We usually think of nickel as a bright silver metal, but it may be plated from certain solutions, as a black deposit. A solution giving black nickel contains nickel and zinc sulfates, cyanide, arsenious acid, ammonia, and ammonium carbonate. This black nickel was used extensively during the war for hardware, harness fittings, and equipment used by the government requiring a dark

FIG. 1.



Electrolytic zinc plant; drawing zinc. Great Falls Reduction Department. Courtesy Anaconda Copper Mining Company.

finish.[2] It may be mentioned in passing that other metals also may be deposited black, *e.g.*, silver, copper, and platinum.

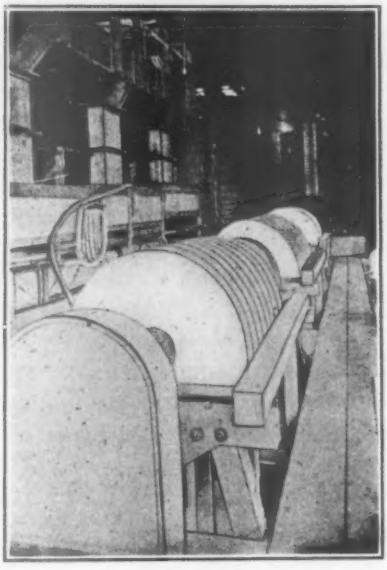
Within recent years zinc and lead have been used extensively for electroplating, especially in the preparation of military supplies. Electroplated zinc has a dull finish which detracts considerably from its appearance compared with ordinary so-called galvanized coatings which are formed by dipping in melted zinc, but they give much better protection. Lead plating has recently been conducted on an extensive scale for lining gas shells and also for plating on the inside of underweight shells merely to increase the

[2] Blum, *Tr. Am. Electroch. Soc.*, **34**, 169 (1919), "Electroplating for Military Uses."

weight, thus salvaging thousands of rejected shells. Other applications such as the lining of chemical apparatus are under investigation, and it is probable that lead plating will be more extensively used in the future. A solution of lead fluosilicate or borate is used.

Until very recently the electrodeposition of alloys was confined

FIG. 2.



Cadmium cells, showing rotating cathodes in place.

principally to electroplating brass. Since zinc and copper, the constituents of brass, have electrolytic potentials far apart in value, it is necessary to use a solution in which the potentials are brought near together. A very complex salt is required, and cyanides are the only ones which give satisfactory deposits of brass.

One of the most recently adopted alloy deposits consists of equal parts of tin and lead. These two metals are so nearly equal in their electrolytic potentials that there is no trouble at all in depositing them together from solutions of their simple salts. In fact, tin cannot be separated from lead by electrolytic refining. The solution is a mixture of lead and tin fluosilicates or fluo-

borates. This lead-tin deposit is used for the lining of air flasks of naval torpedoes.

Other improvements in electroplating have to do with the cleaning of the surface in preparation for plating, this being a most important step in the process. One such method consists in simultaneously cleaning and plating with copper from a hot cyanide bath.[3] The hot alkaline cyanide solution removes the dirt and, wherever clean, a good copper deposit is produced by the current. Another method is to electrolyze as cathode in a hot alkaline solution. The hydrogen evolved reduces oxides and helps to carry off dirt. The scale from sheet iron plates may be removed by electrolyzing as cathode in a hot sulfuric acid reducing the scale to iron in place of blowing it off with hydrogen as is done in ordinary pickling. This would seem to be a much better method of removing the scale than pickling in hot sulfuric acid, which uses up a large quantity of iron and acid.[4] This process is reported to be in use. A rather interesting method of covering aluminum wire for the purpose of insulation may be mentioned here as it is closely related to plating. It has long been known that aluminum electrolyzed as an anode in nearly any solution is soon covered with a thin non-conducting layer of some aluminum compound. In recent years use has been made of this property of aluminum for insulating aluminum wire. The wire is drawn through a sodium silicate solution in which it is electrolyzed as an anode.[5] The thin film produced will stand 200 to 500 volts. This wire is used in coils which require light weight and which are subject to relatively high temperature. Its advantage is the small volume taken up by the insulation.

There have been only a few innovations in electrotyping. The usual procedure is to take an impression in wax and to deposit the metal to be used in printing on this after making the surface conducting with graphite powder. While this is satisfactory for some purposes, it is not sufficiently exact to make substitutes for the steel plates used by the government in engraving bond issues. Such plates, however, have been successfully produced by substituting

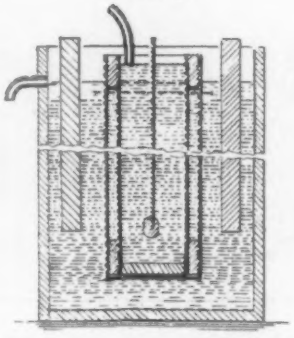
[3] *Tr. Am. Electroch. Soc.*, **27**, 141 (1915).

[4] Hering, *Met. Chem. Eng.*, **13**, 785 (1915); also *Tr. Am. Electroch. Soc.*, **31**, 181 (1917); and *Met. Chem. Eng.*, **17**, 713 (1918).

[5] German Patent, 238,110 (1912); U. S. Patent, 1,289,215; Skinner and Chubb, *Tr. Am. Electroch. Soc.*, **26**, 137 (1914).

for the wax, negatives made by electrodeposition of alternate layers of nickel and copper on the steel engraving to be copied, stripping this from the engraving and then depositing the actual printing plate on this metal negative.[6] The surface must be slightly greased so that the two metal sheets can be separated. The printing plate is made by a deposition first of nickel, .005 inch thick, and then copper and nickel in alternate layers for periods of one hour during six days. Among other galvanoplastic products, more

FIG. 3.



Hybinette vat for nickel deposition. Nickel sulfate solution circulates to cathode in the diaphragm through diaphragms by the nickel-copper anodes and out the overflow.

or less recent, may be mentioned duplicating phonographic records, all the metal decorations on glass and pottery, and the production of bronze statues.

Finally, many soldiers whose faces were disfigured during the war were supplied with artificial faces of thin copper plated on plaster models made from photographs. These copper faces were painted, of course, to look like the original.

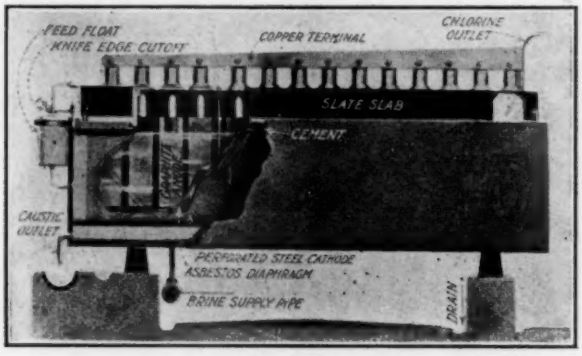
In recent years there have been some notable advances in wet electrometallurgy. Numerous early attempts to extract metals from their ores by methods involving electrolysis ended in failure. Among these may be mentioned the Marchese [7] process, where the attempt was made to produce pure copper by electrolyzing copper matte anodes. The curious thing about the history of this process

[6] Blum, *Tr. Am. Electroch. Soc.*, **39**, Oct. (1921).
[7] *Z. f. Electroch.*, **1**, 50 (1894).

is that the laboratory tests were considered encouraging, and the process failed when tried on a larger scale.

The history of the Siemens process for copper is very similar. The Hoepfner processes for copper[8] and for zinc[9] extraction also failed. The first success of this kind was achieved at Chuquicamata,[10] where copper ore is leached in sulfuric acid, and

FIG. 4.



The Nelson cell for making sodium hydrate and chlorine.

pure copper is deposited electrolytically, using unattackable anodes of fused magnetite or duriron (an alloy of iron and silicon) and copper cathodes. Practically the same process has been extended recently to the extraction of zinc,[11] by depositing zinc from very pure zinc sulfate solutions. Production of electrolytic zinc in quantity began in 1916. A very pure solution is required and some elements must be reduced to about one milligram per litre. Cobalt and chlorine cause the most difficulty. In this case lead anodes may be used, and the cathodes are sheets of aluminum. At first, in some plants, the cathodes were rotated, but stationary cathodes are now universal. The zinc is stripped from the cathodes every 48 hours and remelted. The current density is 25 amperes a square foot. In 1920 there were four plants in this country and one in

[8] *Z. f. angew. Chem.*, p. 160 (1891).

[9] *Metall. u. Erz.*, **10**, 206 (1913).

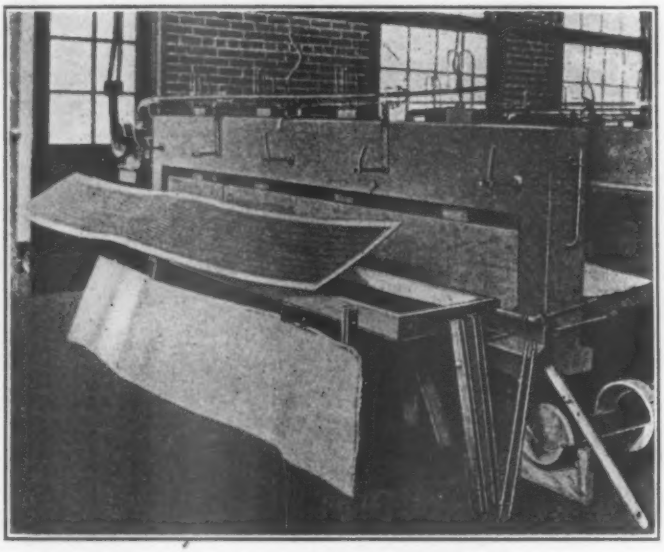
[10] Capelen-Smith, *Tr. Am. Electroch. Soc.*, **25**, 193 (1914).

[11] Ingalls, *Tr. Am. Electroch. Soc.* for 1921; Hofman, "Metallurgy of Zinc and Cadmium," 1922.

Canada producing electrolytic zinc, one in Australia and two in Tasmania.[12] The production in this country is about 10 per cent. of the world's pre-war production.

Cadmium is a metal which occurs only in small quantities in its ores, and production is profitable only where it is a by-product. An electrolytic method for recovering cadmium has been developed

FIG. 5.



The Allen-Moore cell for making sodium hydrate and chlorine.

recently at the mammoth Electrolytic Zinc Plant of the U. S. Smelting, Refining, and Mining Company at Kennett, California.[13] In purifying the zinc solution for electrolysis, copper and cadmium are precipitated by zinc dust. This precipitate has the appearance of a black mud. It is dissolved in dilute sulfuric acid, leaving the copper behind, and is then precipitated on zinc sheets by cementation. This is dissolved in acid cadmium electrolyte, iron and thallium are removed, and the solution is electrolyzed on the rotating aluminum cathodes from which it is stripped. Its

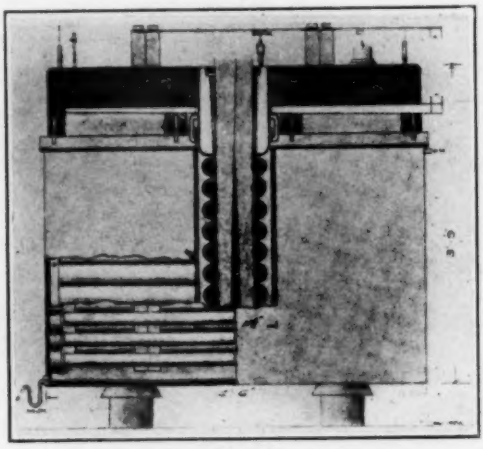
[12] Keeney, *El. J.*, **17**, 206 (1920).

[13] Hanley, *Chem. Met. Eng.*, **23**, 1257 (1920).

uses are as a pigment when changed to the sulfide, and in the metallic state for low melting point alloys.

The following problem is a little different from either recovering metals from ores or refining. This consists in separating the constituents of a copper-nickel alloy. Many ores contain these two metals in about equal amounts, and the smelting process gives

FIG. 6.



The Marsh cell for making sodium hydrate and chlorine.

an alloy of about equal parts. An earlier electrochemical process, due to David H. Brown,[14] accomplished this separation, but a more recent method is the Hybinette [15] process, originating in Norway, and now in use in Canada. In this process the anodes are not unattackable, as in the case of the copper and zinc recovering processes just menioned, but consist of the alloy of nickel, copper and iron. The cathode is a thin sheet of copper or iron with the surface treated so the nickel can be stripped off, and is separated from the anodes by a diaphragm of two sheets of cloth. The nickel sulfate solution circulates to the cathode compartment. This causes a flow through the diaphragm and overcomes the

[14] *Z. f. Electroch.*, **9**, 392 (1903).

[15] *Electroch. Met. Ind.*, **4**, 34 (1906); *Met. Chem. Eng.*, **13**, 249 (1915); *Mining Sci. Press*, **114**, 666 (1917).

migration of the copper which is dissolved with the nickel at the anode. The solution from the anode compartment is passed over pure nickel, causing the copper to precipitate, and this solution circulates to the cathode.

The refining of metals by electrolysis is one of the largest of the electrochemical industries. The principal metals refined electrolytically are copper, nickel, gold, silver and more recently lead, tin, and iron. The production of electrolytic iron was started in this country five years ago, by the Western Electric Company for making iron powder.[16] Their plant at Hawthorne, Illinois, produces 25,000 pounds a week. On account of its brittleness, it is easily ground. The anodes are mild steel and the cathodes polished steel, from which the deposited metal is stripped when it has become ⅛ to ¼ inch thick.

The electrolytic refining of tin was begun in 1916 at Perth Amboy.[17] Originally fluosilicate solution was used, but later it was changed to sulfate of tin.

It occasionally happens that electrochemical methods are given up in favor of purely chemical ones, as in the detinning of scrap. Up to 1907 the caustic soda detinning process dominated the entire field. In this process the tin scrap was packed into iron gauze baskets and electrolyzed as anode in a caustic soda solution with sheet iron cathodes. The tin dissolved, and deposited in a spongy form on the cathode. It was a very troublesome process to operate on account of the close attention required by the electrolyte, and has been replaced to a great extent by the chlorine process.[18]

The most important process in the production of chemical compounds or elements by electrolyzing aqueous solutions is the electrolysis of sodium chloride with a diaphragm separating the anode from the cathode, for the production of sodium hydrate and chlorine. Many cells have been devised for this purpose. Chlorine is a gas and comes out of the cell of itself, but the hydrate must be removed by continuously drawing off the cathode solution. If the hydrate is drawn off too rapidly, the solution will be too dilute, while if the concentration

[16] Stoughten, *Chem. Met. Eng.*, **26**, 128 (1922); *J. Am. Inst. E. E.*, **50**, 596 (1921).

[17] *Tr. Am. Electroch. Soc.*, **38**, 163 (1920).

[18] *Met. Chem. Eng.*, **17**, 187 (1917).

of hydrate becomes high, the hydroxyl irons migrate to the anode compartment, form chlorate, and attack the graphite anodes. In designing an alkali-chlorine cell, the object is to get the hydrate out just as soon as the desired concentration at the cathode can be produced. It was soon found that a good way to accomplish this was to have the cathode made tight against the diaphragm, and have no liquid in this compartment except what filters through from the anode compartment. The electrolyte decomposed at the cathode is thus washed away soon after decomposition. This was done first in the Hargreaves-Bird cell. The Nelson [19] and the Allen-Moore [20] cells, both of recent design, depend on the same principle as the Hargreaves-Bird cell, but differ in construction details. A still later construction of the same type is the Marsh [21] cell, in which the anode and cathode are brought closer together by using graphite rods for anodes with correspondingly fluted cathodes, saving both power and floor space. Another method of removing the alkali is used in the Basel cell,[22] introduced in France during the war. In 1917 these cells were producing nearly half of the total French output of chlorine. In this cell the "propulsive" cathode is placed in a comparatively narrow cathode chamber formed by narrow meshed asbestos fabric. The hydrogen liberated in this small chamber produces in the surface of the electrolyte a froth consisting of bubbles of hydrogen, the shells of which consist of solution of alkali carried up by the gas. This froth is carried away through an overflow.

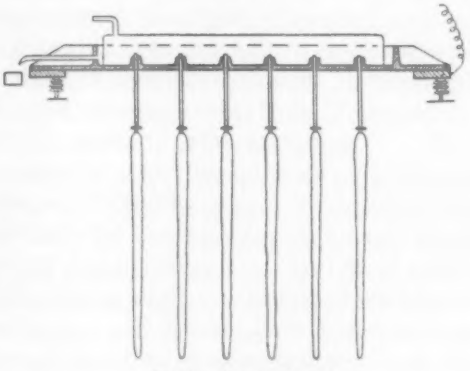
In most electrochemical processes for producing chemical compounds the substance to be acted on is in solution and unattackable anodes are used. The following are two examples where the anode furnishes one of the elements going into the product. A number of years ago the Luckow process for white lead was invented, consisting in electrolyzing lead anodes in a solution of potassium chlorate and carbonate, blowing in a mixture of air and carbonic acid to replace the carbonic acid used up. This, or a similar method, was referred to in 1920 in one of the technical journals [23] as having been the subject of a successful research made for the

[19] *Tr. Am. Electroch. Soc.*, **35**, 239 (1919).
[20] *Chem. Met. Eng.*, **21**, 370 (1919).
[21] *Tr. Am. Electroch. Soc.*, Vol. 39 (1921).
[22] *Chem. Met. Eng.*, **24**, 168 (1921).
[23] *Chem. Met. Eng.*, **22**, 531 (1920), Editorial.

purpose of starting this manufacture in this county, and it is probably now in operation.

During the war there was urgent need for neutral solutions of sodium permanganate. The chemical method of making this is to heat manganese dioxide with sodium hydrate, dissolve the manganate formed and then oxidize to permanganate either by electrolysis in the anode compartment of an electrolytic cell or by means

FIG. 7.



Basel cell cathode unit.

of chlorine or carbonic acid. This was not even as satisfactory as the same method for potassium permanganate, as the yield of sodium manganate on roasting the dioxide of manganese with sodium hydrate is less than the corresponding reaction for the potassium compound, and that has a rather low efficiency. It had been known for a number of years that a ferro-manganese anode electrolyzed in potassium hydrate or carbonate gave a solution of potassium permanganate,[24] but it had not been tried on a large scale. This was done, however, nearly to the point of production, before the Armistice. The anodes were 75 per cent. ferro-manganese, separated from the iron cathode by a diaphragm. Of course, pure manganese would work better than ferro-manganese but this would be too expensive. The principal difficulties were with the anode. They are brittle and could not be cast in large plates because they invariably cracked on cooling, but must be cast

[24] Lorenz, *Z. f. anorg. Ch.*, **12**, 393 (1896).

in bars, a number of which are clamped to an iron piece to form one complete anode. Then some difficulty was found with the tendency ferro-manganese has of becoming covered with an insulating layer of oxides when electrolyzed, but this may be largely overcome by keeping the temperature down. The current efficiency is only about 35 per cent. This low efficiency is due to the fact that part of the current is used to oxidize the iron and only part of the manganese is changed to permanganate.

The process works equally well for potassium permanganate.[25]

The production of organic compounds by electrolysis has had relatively little application in this country, although in Germany a number of compounds such as iodoform, chloral, vanillin, azo and hydrazo compounds and anthraquinone have been manufactured profitably. During the war, however, the impossibility of getting photographic developers from Germany caused the Eastman Kodak Company,[26] among others, to experiment on the electrolytic production of paraminophenol by electrolyzing nitrobenzene suspended in sulfuric acid solution, this having long been known as a laboratory experiment. Four men and 50 cells produced 80 to 100 pounds a week, but it was found too expensive to compete with any chemical process, and was abandoned. The plant was converted to the production of ammonium persulfate when this was in demand by the government.

On the other hand, another company is now manufacturing anthraquinone electrochemically, and it is expected that the electrolytic manufacture of paraminophenol, hydroquinone, and other compounds will be started soon.[27]

It is rumored that in Germany aniline is made by introducing nitrobenzol in the cathode compartment of alkali-chlorine cells. This has two beneficial effects: It saves the evolution of a corresponding amount of hydrogen which is usually wasted, and lowers the cell voltage by depolarization.

Storage batteries and primary batteries have had no very striking developments. The iron clad battery, now about ten years old, is one of the most radical departures in pasted plate storage batteries. The positive lead peroxide plate is the weak part

[25] See *Tr. Am. Electroch. Soc.*, **35**, 371 (1919); *J. Ind. Eng. Ch.*, **13**, 763 (1921); *Chem. Met. Eng.*, **21**, 680 (1919).

[26] *Tr. Am. Electroch. Soc.* for 1921.

[27] Note from Dr. Thatcher of the Kathol Mfg. Co.

of these batteries on account of shedding in the material. In the so-called iron clad battery the positive plate is made by packing lead peroxide in a vulcanite tube perforated with small openings for the passage of the current. A rod of lead runs through the centre of each tube for contact. These positives have a longer life than the ordinary pasted plate. A battery is now made by the Philadelphia Storage Battery Company in which the peroxide plate is protected from shedding by slotted rubber containers, and for which a life as long as that of the iron clad battery is claimed. Within a year a very thin plate battery giving 50 to 200 per cent. higher output per unit weight and with a longer life has been described by C. W. Hazlett.[28] A further advantage of plates only $^1/_{32}$ of an inch thick, as are used in this battery, is that they are so assembled as to make buckling impossible.

Until recently all pasted plates have been filled by hand, using wooden paddles to force the lead oxide paste into the lead-antimony grids. Of late, some manufacturers have developed a machine for this purpose.

The most important primary batteries are Leclanché cells with very little electrolyte, called dry cells. They are used for ignition, flash lights, telephones, and all kinds of open circuit service. Millions of them are made a year in this country. There are two drawbacks to these cells: They are apt to deteriorate even when not in use, and when in use, if too much current is drawn at once, they polarize, as the depolarizer, manganese dioxide, is not very rapid in action. The manufacturers are constantly working to improve this battery, but the results are in general kept secret. One method that has been adopted by some to prevent deterioration before putting in service is to make up the battery perfectly dry [29] and have the necessary water added when it is put in service. A recent French modification is to do away with the manganese dioxide entirely, and use porous carbon in its place, which takes up the oxygen of the air and makes this available for depolarization. This depolarizer is said to be permanent.[30]

There has been important progress during the last few years in electrolyzing fused salts. The largest in these industries, the

[28] *Tr. Am. Electroch. Soc.* for 1921.
[29] *Electrician*, **83**, 605 (1919).
[30] *C. r.*, **172**, 317 (1921).

production of aluminum, increased considerably in quantity during the war, and aluminum is now fourth of the non-ferrous metals as to quantity produced, the order being copper, zinc, lead, aluminum. During the last few years magnesium and cerium were made in quantity for the first time in this country. Calcium production was also started in small amounts, as there is not much demand for this metal in the pure state, but an alloy of lead, calcium, and barium known as Frary metal, is now produced in large quantities for a bearing metal, by electrolyzing a mixture of fused calcium and barium chlorides on a fused lead cathode contained in iron pots.[31] The layer of fused salt is 3 to 4 inches thick. The anode is a graphite rod at the centre. The pots are placed in brick-work fired with coal for melting the lead, and the salt mixture is fused by the passage of the current. There is a tendency towards forming metal fog and calcium and barium carbides, so that three days' electrolysis is required to produce an alloy containing 2 per cent. of the alkaline earth metals. When the proper amounts of calcium and barium have been electrolyzed into the lead, the alloy is drawn off from a whole series of pots and mixed in a large kettle and further alloyed ingredients are added, such as ¼ per cent. of mercury.

Practically all metals made by electrolyzing fused salts are made from a solution of the oxide in some fused salt or from the fused chloride of the metal. In the manufacture of aluminum, aluminum oxide is dissolved in a mixture of fluorides, held in a carbon cell at about 1000° C. The carbon container is the cathode, and graphite anodes are used. Aluminum is collected at the bottom and is removed from time to time. Magnesium is made by the more generally used process of electrolyzing the fused chloride. Magnesium floats in the bath and is ladled out with an iron spoon.

In electrolyzing calcium chloride the metal would burn up if allowed to float around on the surface of the chloride, so it is removed as rapidly as it is produced by allowing it to freeze to the cathode which dips only a short distance into the chloride. The cathode is gradually raised and thus a stick of calcium is drawn out of the bath.

The electrolysis of fused salts is in principle very simple, but just the right conditions have to be found before it can be carried

[31] *Tr. Am. Electroch. Soc.* for 1921.

out successfully, and these are different for each metal. There are also numerous phenomena that appear in the elctrolysis of fused salts that are not understood.

So far only processes in which direct currents are used and the products are obtained by electrolysis have been considered. By far the greater part of electric furnace products are made solely by heat produced by the current. It is in this branch of applied electrochemistry, called electrothermics, that the greatest developments have occurred in the past years.

Before discussing the different products it would be well to mention one or two advances in electric furnaces themselves. The first is a new kind of carbon electrode known as the Söderberg self-baking continuous electrode, perfected in Norway in 1918, and recently installed at Anniston, Alabama.[32]

It is made by feeding continuously unbaked electrode mixture to the furnace and the mass is baked by the heat of the furnace in which it is used. The operation is continuous during the life of the furnace, and the difficulty involved in changing electrodes over a hot furnace is avoided. It is also a more economical electrode. Electrical contact is made as near the roof of the furnace as convenient, when the carbon has become conducting, and encircles an iron casing in which the electrode mixture is held. The casing adds to the conductivity of the electrode, holds the shape and size while new mixture is added, and protects the carbon from oxidation before entering the furnace.

The raw electrode mixture is the same as in ordinary carbon electrodes which are to be baked, consisting of coke, semi-graphitized anthracite, tar, and pitch, finely ground and mixed together at about 80° C. This is stamped into the iron casing. The casing is made in sections, which are riveted or welded to old ones to extend the electrode. The casing is fed into the furnace along with the electrode, and is of course melted off in the furnace. The current density in one of these electrodes is 4.2 amperes per square centimetre in a 34-inch electrode.

This process requires a platform above the furnace.

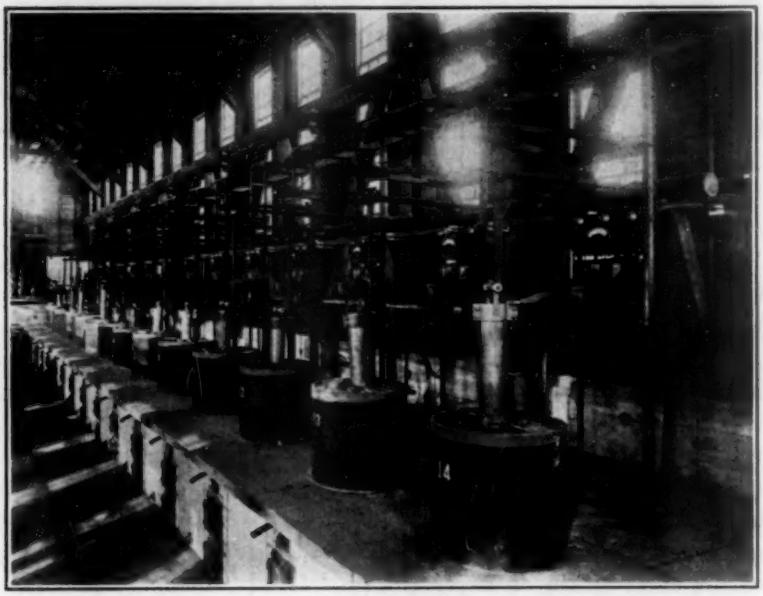
An entirely new type of electric furnace has recently been developed by Professor Northrup in which the heating is produced

[32] Richards, *Tr. Am. Electroch. Soc.*, **37**, 169 (1920); **38**, 351 (1920).

by the eddy currents induced in the material to be melted by a high frequency current.[33]

Coming now to electrothermic products, ferro-alloys are important because of the enormous increase in production between

FIG. 8.



United Lead Company, Frary Metal Plant, Keokuk, Iowa. Cowen, Simpkins & Hiers. Battery of electrolytic pots. Courtesy American Electrochemical Society.

1910 and 1918. In 1910 there were two ferro-alloy plants in the United States and Canada, using 20,000 KVA.

In January, 1920, there were 40 plants using 200,000 KVA, so that at the time of the Armistice the United States led the world in ferro-alloy production.[34] Since then, however, 75 per cent. of these plants have shut down. The two most important developments among the ferro-alloys have been the electric smelting of manganese ores and the increased use of molybdenum in steel.

The electric furnace refining of steel is a comparatively new

[33] *Tr. Am. Electroch. Soc.* for 1921.

[34] Keeney, *El. J.*, 17, 206 (1920).

industry, as it was just beginning 13 years ago, and at the beginning of 1920 there were 1000 furnaces for melting and refining steel built or under construction throughout the world. About one-third this number are Héroult furnaces.[35]

The most recent improvements in the construction of electric steel furnaces have been directed toward shaping the interior so as to lengthen life of the lining. There is such a narrow margin of temperature between the liquid steel and the melting point of the lining that overheating and the action of the slag are very apt to attack the lining rapidly. This difficulty is aggravated if the electrodes are so placed that the lining is heated more at one place than another. In the three-phase Héroult steel furnace the three electrodes are placed in the form of a triangle. In more recent designs of three-phase furnaces such as the Vom Baur and the Ludlam furnaces, the electrodes are placed in a straight line and the contour of the lining made such that at the slag line the temperature is approximately the same throughout.

The electric smelting of iron ore, originally suggested by Sir William Siemens in 1878, has within late years been carried out industrially in Norway, Sweden, Switzerland, Italy and Japan. It was also attempted in this country, but was given up in 1914. Electrolytic pig iron is made only where coke is scarce and water power plentiful.

In France [36] there was a great development during the war of an electric furnace process for converting steel turnings from munition plants into a low carbon cast iron, high in silicon and low in sulfur and phosphorus for the production of cast iron shells. This is called synthetic electric furnace cast iron. While previously low carbon steel has been carburized to high carbon steel, cast iron had never been made in this way. This has also been done in this country.[37]

The electric smelting of zinc has been carried out in Sweden since 1901. Although this has been extensively investigated in this country in recent years, and the chief difficulty, the production of blue powder, has been solved,[38] still no zinc is smelted

[35] See Rodenhauser, Shoenawa, and Vom Baur, "El. Furnaces in the Iron and Steel Industry."

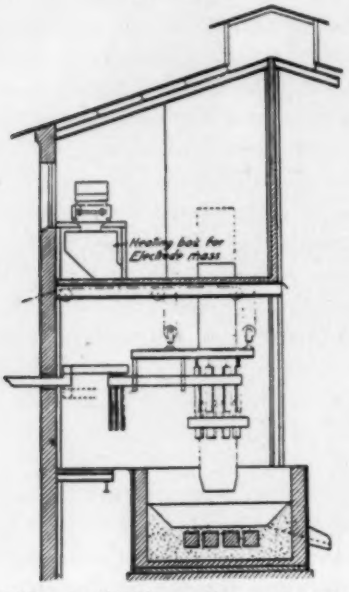
[36] Keller, *Tr. Am. Electroch. Soc.*, **37**, 189 (1920).

[37] *Chem. Met. Eng.*, **26**, 312 (1922).

[38] Keeney, *Elec. J.*, **17**, 206 (1920).

commercially here or in Canada. Whether this method will ever compete in this country with the electrolytic extraction already described remains to be seen. The zinc experts differ in their predictions. It is interesting to note that zinc is the only metal for which serious attempts have been made to employ all three electric

FIG. 9.



Söderberg self-baking continuous electrode.

methods of production—smelting, electrolysis of a fused salt, and wet electrometallurgy.

The use of the electric furnace has in recent years been extended to the brass industry, for melting brass in foundries. By the use of large melting units, with closed melting chambers free from oxygen and products of combustion, electric melting is said to have revolutionized metal handling methods and produces a more uniformly high quality of product, with less labor and less metal loss, than have previously been possible to attain.[39]

The most important of all the electrochemical industries will

[39] St. John, *Tr. Am. Electroch. Soc.* for 1921.

probably eventually be the fixation of atmospheric nitrogen. While in recent years no new process of importance has been invented, an immense amount of research has been carried out to perfect methods already known, especially the fixation by the synthesis of ammonia, called the Haber process. Ammonia is formed when nitrogen and hydrogen are heated electrically to about six hundred degrees in contact with a suitable catalyzer. The history of the development of this process is very interesting. One of the first researches for the purpose of testing this reaction as a means of fixing nitrogen was carried out by Haber and Van Oordt [40] in 1905, with very discouraging results. It was found that at atmospheric pressure, if the temperature were high enough to make the velocity of the reaction have an appreciable value, the equilibrium conditions were very unfavorable, while at lower temperatures where the equilibrium is favorable, the velocity of the reaction was too slow. Still, in spite of the unpromising characteristics of this reaction it was developed during the war in Germany to large scale production.[41] This was done by finding a good catalyzer which allows a lower temperature to be used, and by compressing the gas mixture of nitrogen and hydrogen to something like 200 atmospheres, which improves the yield because there is a volume contraction when ammonia is formed. The ammonia can be oxidized with a high efficiency to nitric acid, by the Ostwald process of mixing with oxygen and passing through a hot platinum wire gauze. The ammonia is first oxidized to nitric oxide which is then passed into water with the production of nitric acid.

During the war a plant was built and operated by the United States Government for large scale synthetic production of ammonia, using a catalyst invented by de Jahn.

A more recent development is the Claude process [42] in which everything is essentially like the Haber process except that the gases are made to react under a pressure of 1000 in place of 200 atmospheres. This increases the efficiency from 13 per cent. by the Haber process to 40 per cent. This process is now in successful operation in France.

Of all methods of fixing atmospheric nitrogen, the absorption by calcium carbide to form calcium cyanamide when heated in an

[40] *Z. anorg. Ch.*, **44**, 341 (1905).

[41] See description of plant at Oppau, *Chem. Met. Eng.*, **24**, 305 (1921).

[42] *Chem. Met. Eng.*, **23**, 22 and 395 (1920).

electric resistance furnace to about 1000° C. is by far the most extensively used. The product is used as a fertilizer or to make ammonia by treating with superheated steam. A further use of calcium cyanamide recently has been developed successfully in this country, while abroad it was more or less of a failure.[43] This consists in changing cyanamide to cyanide by fusing in an electric furnace with sodium chloride. The product is used in the cyanide process for extracting gold and silver from ores.

There is a method of fixing atmospheric nitrogen which produces sodium cyanide directly, known as the Bucher process, consisting in heating sodium carbonate, carbon, and nitrogen in the presence of iron as a catalyzer. This reaction was discovered in 1846, and many unsuccessful attempts were made to use it on a commercial scale. In recent years Professor Bucher [44] has revived interest in it by his extensive researches. During the war a government plant was put up at Saltville, Virginia, to manufacture cyanide by this process, but the heating was done by gas. It is probable, however, that eventually electric furnaces will be used here also,[45] especially as rather careful temperature control is necessary. There is, it seems, no plant making cyanide by this method at present.

Clarification of Sugar Solutions.—In the determination of reducing sugars, their solutions are frequently clarified by treatment with basic lead acetate and removal of the resulting precipitate by filtration. Any excess of lead is then removed by precipitation with a suitable reagent; the solution is filtered and used for the analytical determination. DUANE T. ENGLIS and CHUK YEE TSANG, of the University of Illinois (*Jour. Am. Chem. Soc.*, 1922, xliv, 865–867), added basic lead acetate to solutions of dextrose and fructose, and used aliquot portions for removal of the lead by means of each of the following reagents: Potassium oxalate, potassium sulphate, potassium sodium tartrate (Rochelle salt), sodium carbonate, and disodium phosphate. They studied the adsorption of these sugars in the lead precipitate by determination of the reducing sugar content of the original solution and of the filtrate from the lead precipitate. Disodium phosphate was found to be the most satisfactory reagent for the removal of lead, since it gave rise to a minimum loss of sugar, and almost invariably yielded a clear filtrate. J. S. H.

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[43] Landis, *Tr. Am. Electroch. Soc.*, **37**, 653 (1920).

[44] *J. Ind. Eng. Chem.*, **9**, 233 (1917).

[45] *Chem. Met. Eng.*, **26**, 124 (1922).

CONTRIBUTIONS TO THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE.*

BY

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I. INTRODUCTION.

Historical Considerations.—We are unable to penetrate the archives of the early human race to a date where we may say with assurance that glue was not yet discovered. Certain it is that this material was in use as an adhesive in the days of the great Pharaohs of Egypt. Among the stone carvings of the ancient city of Thebes of the period of Thothmes III, the Pharaoh of the Exodus, and at least 3300 years old, is one depicting the gluing of a thin piece of a rare wood of red color to a yellow plank of sycamore. The carving (Fig. 1) shows a pot of the glue being heated over a fire, and several samples of veneered and inlaid wood. One of the figures is spreading the glue with a brush, and in the lower section the workmen are preparing the thin slabs of veneer.

In the Roman Period mention is made to the value of glue by Lucretius, Pliny, Varro, and Cicero, and in the middle ages Shakespeare and Francis Bacon referred to it.

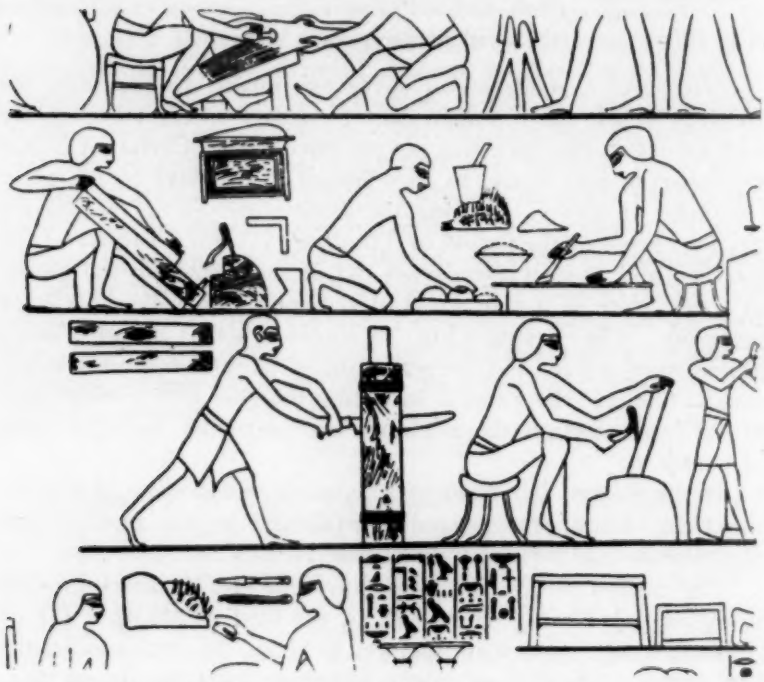
The earliest record of manufacture that can be traced directly from the present day dates back to the time of William III of Holland, where it was manufactured in 1690. In 1754 appears the first mention of glue in patent literature (British Patent 691, May 23, 1754). This refers to the preparation of "a kind of glue called fish glue," made from "the tails and fins of whales, and from such sediment, trash, and undissolved pieces of the fish as are usually thrown away as useless" after extraction of the oil.

The older glues had been made from "the hides of bulls," according to Lucretius and Pliny, and bones were apparently not utilized for the purpose until about 1814, at which time a patent was granted for the treatment of bones with acids, and the con-

* Communicated by Dr. E. R. Weidlein, Director, Mellon Institute of Industrial Research of the University of Pittsburgh.

version of the residue into glue. Steam under pressure "conveyed into a mass of bones in such a manner as to extract therefrom a gelatin adapted for the purpose of glue" was first described in 1822. Sulfurous acid was introduced in 1838, and vacuo evaporation in 1844.

FIG. 1



Veneering and the use of glue in Ancient Egypt.

The first mention of the manufacture of a gelatin for edible purposes is found in a patent by Arney in 1846. He prepared a powdered gelatin "for forming compositions from which may be prepared jellies and blanc-manges; also, when mixed with farina or starch or starchy vegetable flour, for thickening soups, gravies, etc."

The application of "currents of air artificially dried, either by heat or any of the drying compounds in common use, such as concentrated sulfuric acid or fused chlorid of calcium," was intro-

duced in 1847. A few other important mechanical devices for speeding up the cooling of the product, for pulverizing, and for making a nearly anhydrous powdered glue have been added to the installment of the larger factories in recent years, but the operations to-day are otherwise not greatly different from those which were in practice a hundred years ago.

The earliest official record of the United States Government wherein glue is mentioned seems to have been in a compendium of

TABLE I.

Domestic Production, Imports, and Exports of Gelatin and Glue, 1914 and 1919.

1914.

Material	Domestic Production	Total Imports	Total Exports
Gelatin, manufactured	$19,725,703	$875,588	$13,595
Glue		1,725,703	266,334
Mucilage		.....	26,182
Isinglass and Fish Glue		70,212	.....
Total	$19,725,703	$2,755,893	$306,111
Hide Cuttings and other glue stock	no data	$1,510,608	.....

1919.

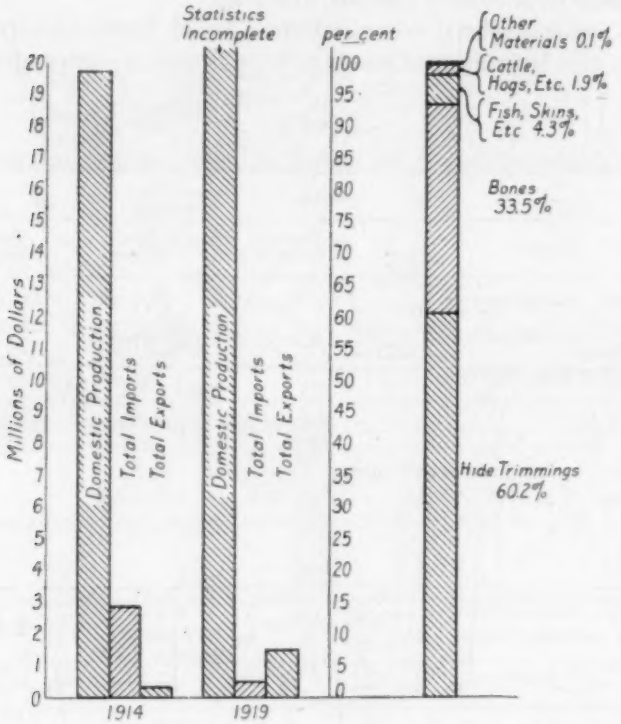
Gelatin, manufactured	no data	$241,835	$1,489,625
Glue and size		208,882	
Total		$450,717	$1,489,625
Hide Cuttings and other glue stock		$978,514	.....

all the manufactures of the several counties of each state which was compiled for the year 1810. In this there are listed six establishments making glue in Pennsylvania, with a total product value for the year of $53,206, and one in Maryland with a product value of $500. In no other state is glue mentioned as being produced.

Comparative Statistics.—The manufacture of glue and gelatin in this country since 1810, and the most recent data available upon imports and exports, are given in the tables, taken

mainly from the Census Reports of the Department of Commerce and the Bulletins of the Bureau of Foreign and Domestic Commerce (especially *Bull.*, **82**, 1919).

FIG. 2.



The domestic production, total imports, and total exports of glue and gelatin for the years 1914 and 1919.

Distribution of glue manufactured from various materials in the United States in 1900.

In Table I and Fig. 2 is shown a comparison of the domestic production, the total imports, and the total exports of glue and gelatin for the years 1914 and 1919. The most striking feature observed here is the enormous increase in exports (about 380 per cent.) and decrease in imports (about 510 per cent.) which occurred in that five-year period.

Table II and Fig. 3 show the number of establishments employed in manufacturing glue or gelatin as their principal product,

the capital invested, and the value of the product, for the census years from 1810 to 1914, and the distribution of manufacture among the several states in the latter year. It is observed that the capital invested and the value of the product have quite steadily increased, whereas the number of establishments has decreased

TABLE II.

*Glue and Gelatin Manufactured in the United States from 1810 to 1914.**

	Number of Establishments	Capital	Value of Product
1914	57	$17,162,000	$13,733,000
1909	65	14,289,000	13,718,000
1904	58	10,673,000	10,035,000
1899	61	6,144,000	5,389,000
1889	62	4,859,000	4,270,000
1879	82	3,917,000	4,324,000
1869	70	1,955,000	1,710,000
1859	62	1,053,000	1,186,000
1849	47	520,000	652,000
1810	7	.....	53,706

Distribution by States for 1914.

Illinois	9	$5,552,170	$3,731,375
Massachusetts	11	2,956,497	2,588,733
Pennsylvania	8	2,820,250	2,028,767
New York	9	2,459,102	2,483,254
Indiana	3	356,295	280,251
All others †	17	3,018,048	2,620,449

*From establishments engaged primarily in the manufacture of glue or gelatin.
†Includes: Ohio, 5 establishments; California, 3; Wisconsin, 2; and 1 each in Connecticut, District of Columbia, Iowa, Kentucky, Main, Maryland, and New Hampshire.

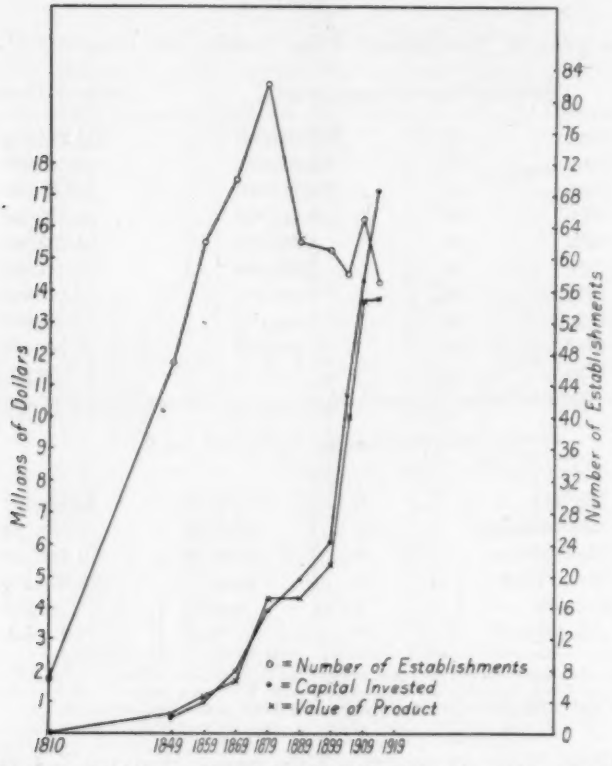
since 1879 from 82 to 57. This means that the industry has become more centralized and that a number of small factories have given place to larger ones. Illinois leads in 1914 in the capital invested and the value of the product, although Massachusetts has a greater number of glue and gelatin establishments.

It is sometimes overlooked that glue and gelatin are also produced in large amounts by establishments that are devoted primarily to the manufacture of some other product. The slaughtering and meat-packing establishments especially produce

large amounts of glue and gelatin, but these are not included in Table II.

Tables III and IV are compiled to give data upon the relative amounts of glue manufactured in glue and in other establishments

FIG. 3.



The glue and gelatin manufactured in the United States from 1810 to 1919.

in 1900 and in 1914, and the relative amount of glue made from the several chief sources, as hides, bones, etc. (See Fig. 2.) In 1900 there was very nearly as much glue made in slaughtering as in glue establishments, but in 1914 only 15.7 per cent. of the value of the total output came from slaughter houses. Five and seven-tenths per cent. came from fertilizer establishments, and 9.0 per cent. from all others, as plants manufacturing sand and emery

paper, tallow, soap stock, food preparations, oleo oil, and fish oil. More than 60 per cent. of all glue (in 1900) was made from hide pieces, fleshings, sinues, leather cuttings, etc., and 33.5 per cent. from bones. Fish skins and refuse contributed 4.3 per cent.

TABLE III.

Distribution of Glue Manufactured in Glue Establishments and in Slaughtering Establishments in 1900.

	Total Pounds	Made from hide trimmings, etc.	Made from bones	Made from cattle, hogs, etc.	Made from fish skins and waste	Made from other materials
Glue Establishments	34,984,448	29,036,901	3,109,165	66,666	2,731,156	40,560
Slaughtering Establishments	34,516,761	12,780,832	20,183,562	1,282,367	270,000	.....
United States	69,501,209	41,817,733	23,292,727	1,399,033	3,001,156	40,560
Percentage Distribution, United States	100.0	60.2	33.5	1.9	4.3	0.1

TABLE IV.

Value of Glue Manufactured in Glue and Other Establishments in 1914.

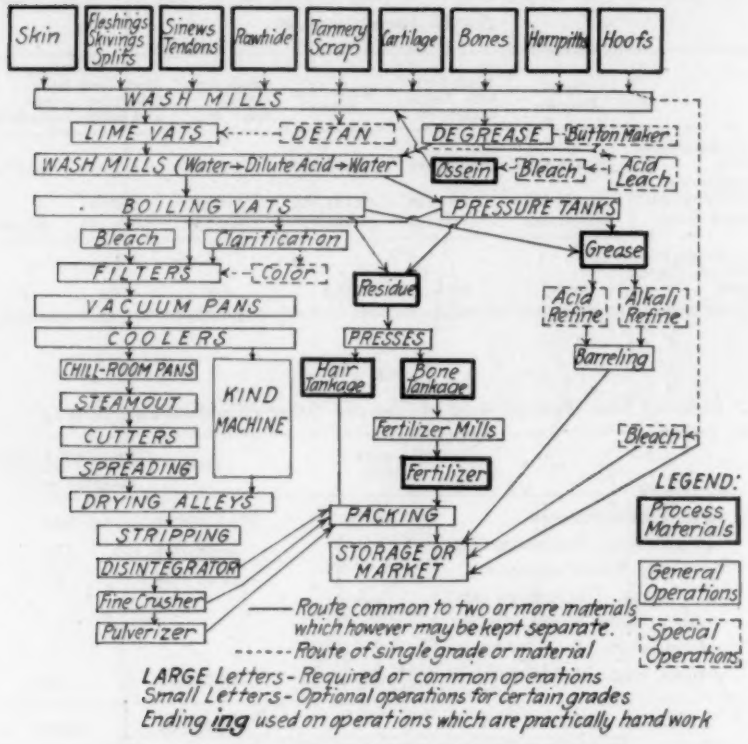
	Quantity pounds	Value	Percentage by value from the different establishments
Glue Establishments	40,844,650	$13,732,824	69.6
Slaughtering Establishments.	no data	3,088,764	15.7
Fertilizer Establishments ...		1,131,243	5.7
All others (including sand and emery paper, tallow, soap stock, food preparations, oleo oil, and fish oil)		1,772,872	9.0
United States		19,725,703	100.0

II. TECHNOLOGICAL ASPECTS.

Manufacturing Operations.—As indicated in the last section, there have been few fundamental improvements in manufacturing operations in recent years. The technic of the operations, the substitution of machinery for hand labor, the selective treatment of different types of stock, and the improvements in control have advanced markedly, however, and much research has been directed towards these ends. It has been one of the aims of the industrial

fellowships at the Mellon Institute to perfect these processes and no effort has been spared in bringing the many steps in the manufacture to a rigidly scientific basis. A given amount of a given stock should produce a definite predetermined quantity of product

FIG. 4.



The operations in the manufacture of glue (by R. C. Shuey).

of a particular grade, and any failure to do so must be regarded as an indication of inefficiency at some stage in the operations. A graphic illustration of the several steps in the manufacture is shown in Fig. 4.

It has been shown that different types of stock will produce different qualities of product, and this has necessitated a careful separation of the various animal parts which find their way to the glue or gelatin manufacturer. If a product of specified properties

is desired, a particular type of stock, treated in a specified way, must be employed. Hide pieces, fleshings, and sinews each give their own type of product, and the hides of oxen, calves, sheep and other animals are kept separate for the same reason. Dense bones react differently from porous bones, and the ossein obtained by dissolving the mineral matter of bones prior to making into glue or gelatin produces a much higher grade of material than the untreated bones. These facts are all taken advantage of in manufacture.

Even the thoroughness of washing stock is a matter of no little concern, for it has been demonstrated that the presence of blood or other albuminous substances imparts to the product properties which are not desired. (*Cf.* section IV.)

It has been common practice for a great many years to allow all hide, fleshing, sinew, and ossein stock to stand in vats of a suspension of lime in water for from four to twelve weeks, with two or three changes, before cooking the material. This operation has been known to plump or swell the stock to many times its original volume, and upon heating with water a much more rapid solution took place. It has also been shown that the lime treatment dissolves mucinous and albuminous substances which may be present, and leaves the collagen which, on hydrolysis, is converted into gelatin.

Some attempt has been made to substitute other material for lime, and not without some degree of success. Acids have been found to produce a swelling in a shorter period of time, but the foreign proteins are not dissolved by acids. Other alkalies and alkaline substances have also been used, and while a proper control results in good yields, the greater cost makes them of questionable value for replacing lime. From a study of recent work on swelling (*Cf.* section IV) it is apparent that the optimum results are obtainable at certain concentrations of H-ion, and as long as such concentrations are attained *and maintained* it is a matter of more or less indifference what acids or bases are used. A saturated solution of calcium hydroxid possesses about the most favorable OH-ion concentration, and has the additional attribute of being only slightly soluble, so that as the OH-ion is absorbed by the stock more will as steadily be supplied by the solution of undissolved lime, so that a constant alkalinity is maintained. This

is of the greatest importance, as the control is rendered entirely automatic.

The excess of lime is removed as far as practicable by washing, and usually some acid is added to assist in the process. Sulfurous acid is especially valuable for this purpose as it serves also as a bleach and a disinfectant. Phosphoric acid is not well adapted as it has been found to favor the production of an insoluble gelatin phosphate. Cloudy and flocculent precipitations have been many times traced to this cause.

It is generally agreed that the "boiling" operation should be conducted in a slightly acid solution, but conclusive tests have not yet been made to settle this point. Experiments are at present being conducted at the Mellon Institute from which it is hoped to solve this question. The most favorable conditions of temperature and duration of heating are also being investigated.

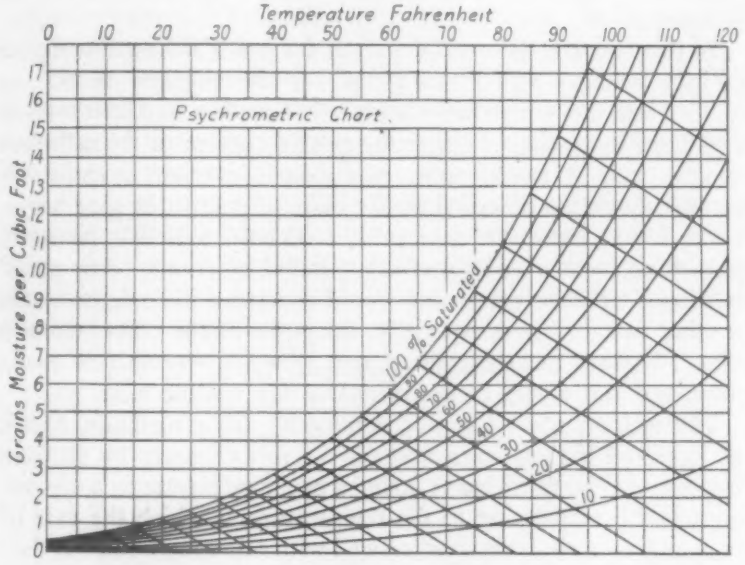
The dissolved glue or gelatin may be filtered, if desired, through loosely packed paper pulp, or it may be clarified by the addition of a little albumin to the cool solution, and the latter then warmed till the albumin coagulates. Upon settling, the albumin carries down suspended material, leaving a very clear sparkling product.

After concentration in vacuo the liquid may be dried in any of several ways. The older method was to allow pans of the liquid to gel in a cold room, cut into sheets with wires, place on nets, and dry in an alley through which warm air was circulating. A great improvement over this method was the introduction of the Kind-Landesmann machine consisting of an endless belt a yard wide upon which the glue was poured in a thin layer. The belt travelled slowly through a cold chamber, causing the glue to gel, and the gel was then transferred mechanically to the nets, and dried in the alleys as before. Some glues are dried by revolving slowly in the liquid a large steel drum heated with steam on the inside. The glue adheres to the drum in a thin layer, and in the course of one revolution is dried and scraped off. Spray drying is a method that offers many inducements, but up to the present has not been largely used. The liquid is simply injected as a spray into a warm low pressure compartment. The water evaporates almost instantaneously, leaving minute hollow spheres of dry product. This is practically cold-water soluble.

The most favorable conditions for drying of the jelly in the

alleys have been studied in detail at the Mellon Institute. Methods for a rigid control of humidity and temperature have been developed, and psychrometric curves prepared by R. C. Shuey (Fig. 5) may be used to much advantage in determining the most favorable temperature for a given humidity, and the maximum efficiency, of any given set of drying conditions.

FIG. 5.



These are but a few of the most important advances that have been made in the technical operation of the glue and gelatin plant.[1]

Evaluation.—The chaotic condition of grade specification in gelatins and glues has been a source of the greatest annoyance to artisans and chemists alike, and the writer has given much time to the establishment of standard tests[2] which will not only differentiate the products consistently, but which will be based upon some fundamental property, will be easily and rapidly made, and

[1] For a more complete description of modern manufacturing operations the reader is referred to the author's treatise, "The Chemistry and Technology of Gelatin and Glue," to be published by the McGraw Hill Book Co. of New York, 1922.

[2] R. H. Bogue: *J. Ind. Eng. Chem.*, **14** (1922), 435.

will be capable of expression in simple and readily understood terms.

A great many methods have been described for the testing of glues and gelatins. These include numerous procedures for measuring viscosity, jelly strength, melting point, and gelatin content. In each case it was assumed that the method was correct in principle, and all that was required was the perfection of the technic. Except in a few instances there was no legitimate basis for the assumption.

In this country the usual criterion for grade is based on either the jelly strength at 10° to 15° C. or the viscosity at 60° or 80° C. But the writer has shown [3] that neither of these tests is in all cases indicative of either the gelatin content or the adhesive strength, and it would seem that gelatin content or adhesive strength should be regarded as the basis of gelatin or glue value. It was found, however, that gelatin content, adhesive strength, and melting point were all perfectly parallel functions. Any measure of one of these properties would therefore indicate correctly the other two, or, more especially, the order of the other two in a series. Neither gelatin content nor adhesive strength is easily determined and would be impracticable for routine tests.

The melting point test was studied by many methods, and it was observed that the measurement of this property by plotting a viscosity-temperature curve, using a capillary pipette as a viscosimeter, and extrapolating to the temperature at which the rate of flow would be zero, corresponded well with other methods. It then became apparent that the extrapolation below 32°–35° C. was unnecessary, and that a viscosity measurement at that temperature resulted in an exactly similar differentiation.

A simple and accurate method for grading was thus obtained. The final perfection of technic involved the use of the MacMichael viscosimeter, the viscosity in centipoises of an 18 per cent. solution (dry basis), at 35° C. being noted. The conversion of MacMichael degrees to centipoises is easily done, after a preliminary calibration against a liquid of known absolute viscosity, as castor oil, by a mere glance at a conversion curve. This being a straight line makes errors of observation improbable, and a setting of the instrument may be made at which the readings indicate directly in absolute units.

[3] R. H. Bogue: *Chem. Met. Eng.*, 23 (1920), 61, 105, 197.

We have, then, instead of the multitudinous array of devices for determining grade, a standard instrument; the measurements are rapidly and accurately made; the results express actual value in reference to either gelatin content or adhesive strength; and the data are expressed in absolute units which are easily understood. For convenience the grade may be written as centipoises, divided by ten, placed after a letter referring to the type of stock used. Thus, H_{12}, B_5, G_{15} would signify respectively, a hide glue of viscosity between 120 and 129 centipoises; a bone glue of 50 to 59 centipoises; and a gelatin of 150 to 159 centipoises.

The H-ion concentration has been shown (*Cf.* section IV) to be of much value in specifying the properties of gelatin, and is therefore introduced as a regular test, to be made by either electrometric or calorimetric means on a 1 per cent. solution.

Other tests may be made to determine the adaptability of any given product to a particular service. These tests, as for grease, foam, jelly consistency, clarity, etc., should be made only when necessary to fulfil specifications, and should be carried out by standard procedures.

III. ECONOMICAL ASPECTS.

Glue Room Economy.—The extent of the waste[4] in glue due to unintelligent handling in the glue rooms of the consumers is difficult to estimate, but it is of very great proportions. It seems indeed incredible that workmen who have handled glue for a score or more of years should be so uninformed of the fundamental properties of the material. A few of these points will make the meaning clear.

A 12-quart pail will hold from 6 to 15 pounds of dry glue, depending on the thickness and size of the flakes. If ground, it will hold from 12 to 21 pounds. But very often glue batches are made up by volume instead of weight.

There is often no standard of viscosity for applying a glue. A workman will add water to satisfy his own judgment. And the temperature both of the wood and glue may be almost anywhere between 30° and 90° C. The viscosity variations with such changes in temperature are enormous.

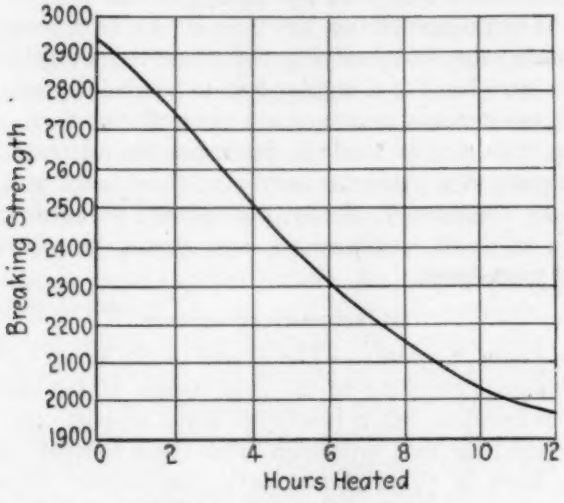
The glue is often but partially soaked in cold water before heating, and some portions not soaked at all. An excessive tem-

[4] *Cf.* R. H. Bogue: *Chem. Met. Eng.*, **25** (1921), 443.

perature and prolonged heating is then necessary to bring the glue into solution.

The temperature used in bringing the swollen glue into solution is frequently so high that hydrolysis breaks the material down to proteoses and peptones. This hydrolysis injures severely the quality of the product. And the glue is usually allowed to remain at a high temperature for many hours at a time, and the injury is of course proportional to both the temperature and the time.

FIG. 6.



Effect of heating on breaking strength.

The matter of losses in glue due to overheating were of such great importance that a number of experiments were conducted to study the exact nature and extent of the losses.[5] It was found that at 80° C. a high-grade glue (H_{14}) was brought down to the equivalent of a low-grade glue (H_5) in twelve hours. In actual adhesive strength the loss was from 2900 to 1900 pounds per square inch, or about 85 pounds per square inch per hour. This is shown in Fig. 6.

That this is not exceptional is shown by reports of Linder and Frost,[6] who obtained a loss in strength of 30 to 45 per cent.

[5] R. H. Bogue: *Chem. Met. Eng.*, 23 (1920), 197. *Veneers*, 15, No. 1 (1921), 30.

[6] Linder and Frost: *Eng. News*, 72 (1915), 178.

by heating a glue at 65.5° C. for 20 hours, and of the Forest Products Laboratory,[7] who obtained a loss in strength of approximately 50 per cent. by heating at 80° C. for 7 hours. The most favorable temperature was found by the latter to be at 60° C., for at lower temperatures bacterial decomposition becomes very rapid.

In spite of the unmistakable significance of these figures, however, the glues in many consuming plants are kept at high temperatures for long periods of time, enough being made up each morning to last through the day, and the residue of one day's run mixed into the batch for the following day. The reason why failures are still few under such conditions is that the consumer buys on a very high margin of safety, even 100 per cent. or more above the required strength. But such a procedure cannot be regarded as economic.

Even in the making of the joint there is possible a vast range of binding strength depending upon the pressure of joining. It was shown in the writer's laboratory [8] that an increase in strength from 800 to 1400 pounds per square inch in one case, and from 1900 to 2500 in another case, was obtained by increasing the joining pressure from 10 to 100 pounds per square inch. A further increase in the latter to 1000 pounds resulted in a further increase in strength to 1800 and to 3000 pounds per square inch, respectively. These data are illustrated in Fig. 7. The reason for this has been found to be only in the perfection of the contact between the two pieces of wood. The bond lies in the tensile strength of the fibrils of dry glue which run from the pores in one piece of wood to those in the other, and the complete elimination of the solid layer of glue *between* the two pieces seems desirable. This is accomplished by high pressure.

In some glue rooms the bacterial decomposition is at all times so far advanced that it is repelling to the senses to enter. Such conditions have even come to be regarded as a necessary part of glue handling. But it is absolutely indefensible and economically disastrous. In such places there is little or no effort made towards cleanliness. Glue pots are never washed or sterilized; the floor is not cleansed of its accumulating mass of spillings; fresh sweet glue is melted in pots containing putrid material; everywhere is

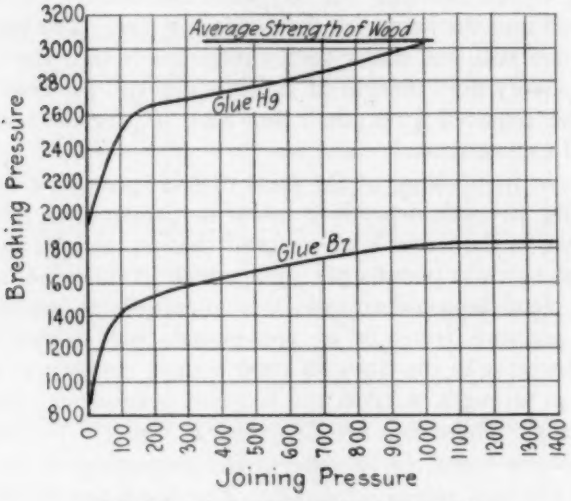
[7] U. S. Forest Service: *Technical Notes*, 104 (1920).
[8] R. H. Bogue: *Loc. cit.*

decomposition. Fresh milk will not keep sweet if put in sour bottles, and neither will glue.

But sour glue is not merely glue that does not smell good. It is rendered inferior by bacterial hydrolysis. A high grade of glue may be made almost valueless by a day of intensive degradation.

Applications in the Industrial Arts.—In carrying out one of the objects of the Institute, namely the dissemination of knowl-

FIG. 7.



Effect of joining pressure on breaking strength.

edge, it has been found desirable, from time to time, to place special information directly before certain groups of people or trades that they may be informed of the progress of the science insofar as it is of direct interest to such groups. To this end a number of papers have been published in various industrial periodicals which have presented matter of interest to the several branches of manufacture represented thereby.[9]

[9] R. H. Bogue: "Glue Losses Due to Overheating," *Veneers*, **15**, No. 1 (1921), 30; "Gelatin in Ice Cream," *The Ice Cream Review*, **5**, No. 1 (1922), 20; "The Dietary Value of Gelatin," *The American Food Journal*, **17**, No. 2 (1922), 39; "Water Resistant Glues: Casein and Blood Albumin," *Chem. Age*, **30** (1922), 103; "Isinglass," *Chem. Age*, **30** (1922), 183; "Edible Gelatin," a series of seven papers in *The Candy Manufacturer*, **2** (1922), May to November; "Glue as an Adhesive," and "Glue Room Economy and Technology," *The Canadian Woodworker*, 1922, May to September.

While a detailed account of the many applications of glues and gelatins in the arts would be out of place in this paper, it will be of value as an aid to a proper understanding of the scope of our problem to point out that these products are used extensively in the following arts and processes:

As a binder for matches, sand and emery papers, abrasive wheels, rubber cements, artificial leather, moulding material, billiard balls, composition cork, imitation hard rubber, and calcimine. As a size for wall papers, writing papers, cotton, wool, and silk fabrics, straws, barrels, walls, etc. As a colloid gel for printing rollers, hectograph plates, artificial silks, artificial ivory, gelatin veneers as marble, travertine, malachite, mother-of-pearl, etc., and in making frosted glass. As a protective colloid for electrometallurgical processes, rubber, pickle baths, foamite, india ink, insecticides, photolithographic plates, and photographic emulsions. In addition gelatin finds service as a food, as a protective colloid and emulsifying agent in dietetics, as a binder and protective colloid in ice cream and jellies, in court plaster, capsules, and pharmaceutical preparations.

Gelatin as a Food.—The value of gelatin as a food is of such importance as to justify a few paragraphs at this place. For in the light of the statement so often heard that gelatin is not a complete protein, it is looked upon with indifference by dieticians, and on account of its unrefined relationship with glue, is too frequently regarded by the housewife as an impure product.

It requires, therefore, to be emphasized that although gelatin is not a complete protein, yet neither is albumin or fibrin or many other isolated proteins, but this does not detract from its desirability as one constituent of a balanced diet. Kirchmann [10] has reported that if gelatin is included in the diet to the extent of 12 per cent. of the required energy, the decomposition of body protein, or the requirement of other proteins necessary for equilibrium, is lessened by 27 per cent., and Krummacher [11] has found that 33 grams of gelatin will spare 14 grams of protein. Murlin [12] observed that protein nitrogen might be replaced by gelatin up to a half of the starvation requirement, while as much

[10] J. Kirchmann: *Z. Biol.*, **40** (1900), 54.
[11] O. Krummacher: *Ibid.*, **42** (1901), 242.
[12] J. Murlin: *Proc. Am. Physiol. Soc.*, **29** (1904).

as two-thirds may be replaced provided carbohydrates are present in such amounts as to provide a half to two-thirds of the total calorific requirement. Kauffman [13] has concluded that the failure of gelatin as a complete protein lies in the absence in its molecule of the three important amino acids, cystine, tyrosine, and tryptophane.

In addition to the value of gelatin as a producer of energy and a sparer of nitrogen, it unquestionably serves as a protective colloid and an emulsifying agent.[14] In natural milk, lactalbumin serves as the protective colloid preventing the coagulation of the casein, but woman's milk contains more than twice as much lactalbumin as cow's milk, while the latter contains nearly three times as much casein. In the infant's stomach the casein of cow's milk is rapidly coagulated by the acid of the gastric juice, but the addition of a little gelatin tends to retard this and to make the coagulum more finely dispersed. What is thus obvious in infant feeding is undoubtedly significant also in the normal dietary.

As an emulsifying agent gelatin tends to keep the fat in a finely divided condition. When casein is precipitated it carries down with it a considerable portion of fat, and troubles that have been experienced by the appearance of undigested fat have been relieved by the addition of gelatin.[15]

IV. PHYSICO-CHEMICAL RESEARCH.

Special Properties of the Colloid State.—Many studies have been reported in the past few years upon the viscosity, swelling, gelation, osmosis, etc., of protein systems. Wolfgang Ostwald has spoken of viscosity as a measure of the colloidality of a substance, and the mathematical conditions upon which the viscosity is dependent have been set forth by Einstein [16] and Hatschek.[17]

So long as the particles of dispersed phase occupy so small a proportion of the total volume of the system that they do not touch each other, the increase in viscosity is a linear function of the

[13] M. Kauffman: *Arch. Physiol.* (*Pflüger's*), **109** (1903), 440.

[14] *Cf.* J. Alexander and J. Bullowa: *J. Am. Med. Assoc.*, **55** (1910), 1196; A. Jacobi, *Ibid.*, **51** (1908), 1216; J. Alexander, *Z. Chem. Ind. Kolloide*, **4** (1909), 86; **5** (1909), 101; **6** (1910), 197.

[15] Moore and Krombholz: *J. Physiol.*, **22** (1908), 54.

[16] A. Einstein: *Ann. Physik*, **19** (1906), 289.

[17] E. Hatschek: *Kolloid-Z.*, **7** (1910), 301; **8** (1911), 34.

concentration and independent of the size of the particles. The equation is then written:

$$\eta' = \eta\,(1 + kf),$$

where η' is the viscosity of the system, η the viscosity of the continuous phase, f the ratio of the volume of the dispersed phase to the total volume of the system, and k a constant which was found by Einstein to be 1; by Hatschek to be 4.5; and by Bancelin to be 2.9.

Just as soon, however, as the ratio of the volume of dispersed phase to the total volume of the system becomes so great that the particles touch each other, then the viscosity concentration curve no longer remains linear, but becomes curvilinear. Under these new conditions the viscosity is expressed, according to Hatschek, by the equation:

$$\eta = \left(\sqrt[3]{A} \,/\, \sqrt[3]{A} - 1\right),$$

in which η is the viscosity of the system, and A the ratio of the total volume of the system to the volume of the dispersed phase. Since we cannot measure directly the dispersed phase volume the value of A may be obtained by the rearrangement:

$$A = \left(\eta \,/\, (\eta - 1)\right)^3,$$

and if the amount of dispersed substance is expressed in percentage, *e.g.*, total volume divided by dispersed weight, then this value, which Hatschek calls A', should bear a constant ratio to A, or

$$A' \,/\, A = K.$$

This ratio has been rigidly tested in the writer's laboratory [18] with the result that the value K was found not to be constant, but to rise regularly to a maximum and thereafter to fall as regularly.

To explain this it was pointed out that the ratio A'/A is in reality an expression representative of the volume occupied by unit weight of dispersed phase. This apparent increase to a maximum may be attributed to a failure of the formula to apply at low concentrations, that is, the particles do not touch, but at higher concentration there is little doubt from the evidence given

[18] R. H. Bogue: *J. Am. Chem. Soc.*, **43** (1921), 1764.

that an actual decrease in volume of particle takes place. This was explained by the writer as due to the resistance of the liquid medium to being drawn out into very thin films. As each particle of gelatin tends to take up water to attain its maximum volume, the liquid phase must be drawn into even thinner and thinner films, and such a process is opposed by the surface tension of the liquid. An equilibrium is therefore produced:

Surface tension (of d.m.) $\rightleftarrows$ *Solvation potential (of d.p.)*

The extent of this influence was found to be expressed by the equation:

$$\sqrt[n]{V^{\circ}_m} - \sqrt[n]{V_m} = s,$$

where V°_m is the volume of dispersion medium when A'/A is at its maximum, V_m is the volume at any other concentration, and s is the decrease in volume per unit weight of dispersed phase at the concentration V_m. n was found to lie between 3 and 4 for gelatin sols.

The swelling, solution and gelation of gelatin have been studied by Martin Fischer and his collaborators.[19] They reported results upon the effects of the several phosphates, citrates, and carbonates of sodium on the above-mentioned properties, but failed to determine the hydrogen ion concentration of the solutions employed.

The effect of hydrogen ion concentration on the properties of gelatin has been emphasized by Loeb [20] and others, and the writer has contributed to this problem by studies not only with pure acids and bases,[21] but with alkali salts.[22]

A typical curve illustrative of the effect of a monobasic acid (hydrochloric) and a monoacid base (sodium hydroxid) on the swelling and viscosity of gelatin is shown in Fig. 8. The curves for gel strength are quite similar.

The behavior of several silicates of sodium which varied in their soda-silica ratio from 1 : 4 to 1 : 1 was especially studied. It was observed that the swelling and other properties of the gelatin increased as the proportion of Na_2O in the silicate molecule of the added solution increased, even though the actual weight of Na_2O

[19] Fischer and Hooker: *J. Am. Chem. Soc.*, **40** (1918), 272; Fischer and Coffman: *Ibid.*, **40** (1918), 303.

[20] Jacques Loeb: *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559.

[21] R. H. Bogue: *J. Am. Chem. Soc.*, on press.

[22] R. H. Bogue: *J. Ind. Eng. Chem.*, **14** (1922), 32.

added was the same in all cases. But this was adequately accounted for by the finding [23] that the hydrolysis of these silicates increased as the ratio $Na_2O : SiO_2$ increased. The OH-ion concentration accordingly increased in a similar manner, and the observed variation in swelling, viscosity, etc., of the gelatin was shown to be proportional to the *pH* of the solution.

The swelling and viscosity reach their maximum values at a *pH* of about 8.5 and 3.5, and decrease at higher or lower values. The jelly consistency, however, is high at *pH* values between 5.0 and 8.0 and between 4.5 and 3.5, but at 8.5 and at 3.0 it becomes lower, and is liquid above 9.0 and below 2.5. From this it is argued that gelation is largely dependent upon the tendency of the gelatin to become solvated, the volume occupied by unit weight of dispersed phase being the determining factor. When this volume is small or large the jelly consistency will be low, but at intermediate values of volume per unit weight, the jelly consistency will reach its maximum.

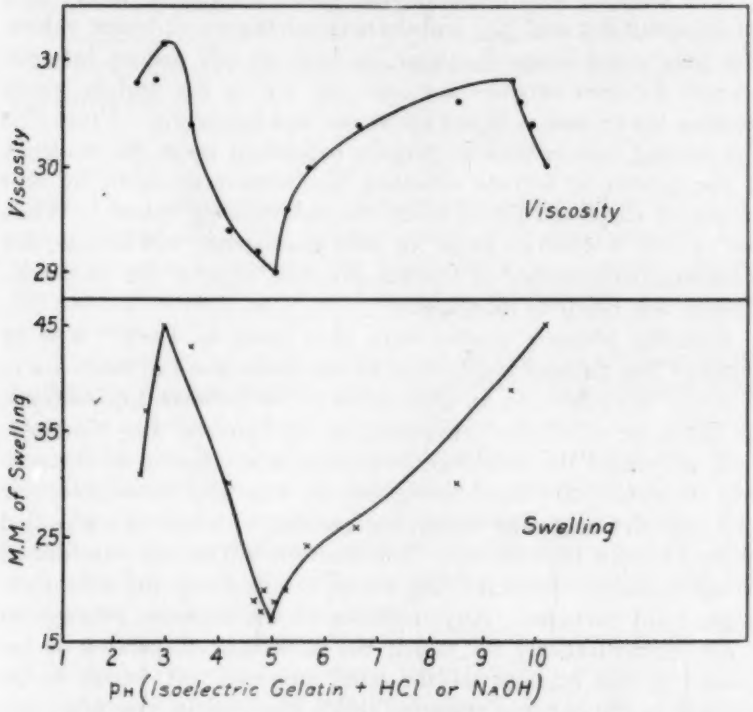
Osmotic pressure studies have been made by Loeb [24] and by Smith.[25] The outstanding feature of this latest work of Loeb lies in its ability to explain, by an application of the Donnan Equilibrium, the influence of H-ion concentration on osmosis and viscosity. Loeb postulates the existence in any protein solution of molecularly dispersed particles floating side by side with submicroscopic solid particles occluding water, the amount of which is controlled by the Donnan Equilibrium. The osmotic effects are determined by the molecular particles; the viscosity effects by the submicroscopic solid particles. Any influence in the solution (change in H-ion concentration) by which the molecular dispersion is increased at the expense of the solid particles will result in an increase in the osmotic pressure and a decrease in viscosity, and the opposite conditions would result in the reverse of these effects.

Of the most profound importance to an understanding of the behavior of the proteins are the brilliant experiments of Loeb by which he demonstrated their amphoteric character and defined in terms of H-ion concentration and valency the influence of added substances.[26] He argued, supported by many experiments, that

[23] R. H. Bogue: *J. Am. Chem. Soc.*, **42** (1920), 2575.
[24] Jacques Loeb: *J. Gen. Physiol.*, **3** (1921), 827; **4** (1921), 73, 97.
[25] C. R. Smith: *J. Am. Chem. Soc.*, **43** (1921), 1350.
[26] Jacques Loeb: *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559.

the so-called Hoffmeister and Pauli series of ions no longer existed in an unexplainable sequence provided only that the concentration of H-ions and the valence were properly considered, and he showed conclusively that gelatin could exist in three forms. At *pH* of 4.7 gelatin was isoelectric, and in that condition was nearly union-

FIG. 8.

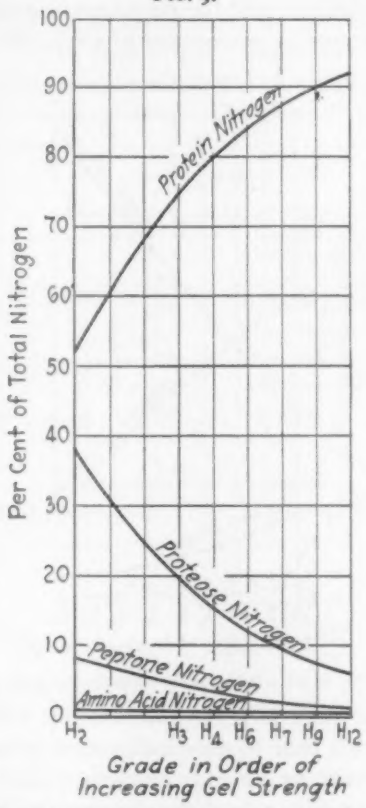


Influence of hydrogen ion concentration on the swelling and viscosity of gelatin.

ized, insoluble, and incapable of combining with the ions of inorganic salts. At *pH* less than 4.7 gelatin existed as cation, and in that condition could combine with the anions but not the cations of added salts. At *pH* greater than 4.7 gelatin existed as anion, and in that condition could combine with the cations but not the anions of added salts. All ions produced a depressing effect on the swelling, but monovalent ions had the least effect. H and OH ions increased the swelling only in that they resulted in an increased ionization of the gelatin.

Constitution.—There has been but a surprisingly small amount of work done upon the chemical composition and constitution of gelatin. Trotman and Hackford [27] developed a relationship between the "gelatinose" precipitated in a saturated solution of zinc sulfate, and the consistency of the jelly producible. This

FIG. 9.



Variation in gel strength with composition. Hide glue.

method of examination has been extended by the writer to include a determination of protein, proteose, peptone, and amino acids.

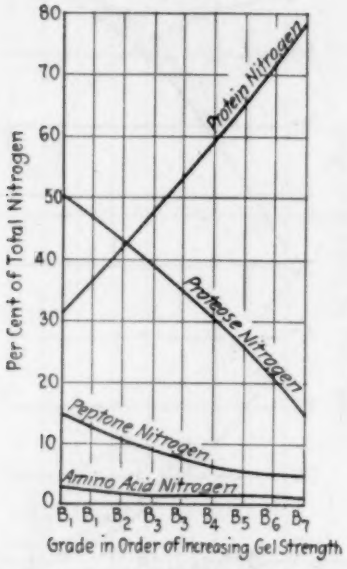
A large number of glues and gelatins of all grades were examined for these constituents [28] by the following procedure. The protein and proteose were precipitated together at the isoelectric

[27] Trotman and Hackford: *J. Soc. Chem. Ind.*, **23** (1904), 1072.

[28] R. H. Bogue: *Chem. Met. Eng.*, **23** (1920), 105.

point with saturated magnesium sulfate solution. The protein was precipitated from another portion with a half-saturated solution of the salt. The nitrogen was determined in each and by difference the proteose nitrogen calculated. The amino acids were determined by Sörensen's formaldehyde titration method in the filtrate from the protein and proteose precipitation. The total nitrogen was determined, and the peptone calculated by difference. Results were expressed as percentage of total nitrogen.

FIG. 10.



Variation in gel strength with composition. Bone glue.

The data show very well the relationship which the products of protein hydrolysis bear to the undegraded protein as the grade, expressed in viscosity at 32° C., changes. The curves for hide glues are shown in Fig. 9 and for bone glues in Fig. 10. The high-grade product is shown to have from 80 to 90 per cent. of its nitrogen in the form of protein, the balance being mainly proteose. The low grades may have as little as 30 to 50 per cent. of their nitrogen in the form of protein. A strong gelatin or glue is, therefore, one in which the nitrogen is mostly in the form of undegraded protein, and as this protein becomes hydrolyzed into proteose, peptone, etc., the strength of the product as regularly decreases.

The ultimate amino acid composition of gelatin has been reported by Emil Fischer [29] and others, but it was conspicuous that the amount of nitrogen accounted for by these esterification methods was only from 40 to 70 per cent. of the total. Recently, however, Dakin [30] has greatly perfected the older methods of separation originated by Fischer, and has succeeded in the remarkable recovery in pure form of 91.31 per cent. of the total nitrogen. Van Slyke and Hiller [31] have lately pointed out that there is a considerable amount of an unidentified base in the hydrolysis products of gelatin. The data of Dakin are shown in the following table:

TABLE V.

Amino-acid Content of Gelatin.

Glycine	25.5	Tyrosine	0.01
Alanine	8.7	Proline	9.5
Valine	0.0	Hydroxyproline	14.1
Leucine	7.1	Tryptophane	....
Serine	0.4	Histidine	0.9
Aspartic acid	3.4	Arginine	8.2
Glutamic acid	5.8	Lysine	5.9
Cystine	....	Ammonia	0.4
Phenylalanine	1.4		

The elementary analysis of gelatin was shown by Procter [32] to be:

C	50.06
H	6.79
O	24.79
N	18.36

from which he deduced the formula:

$$C_{55}H_{87}O_{18}N_{11}$$

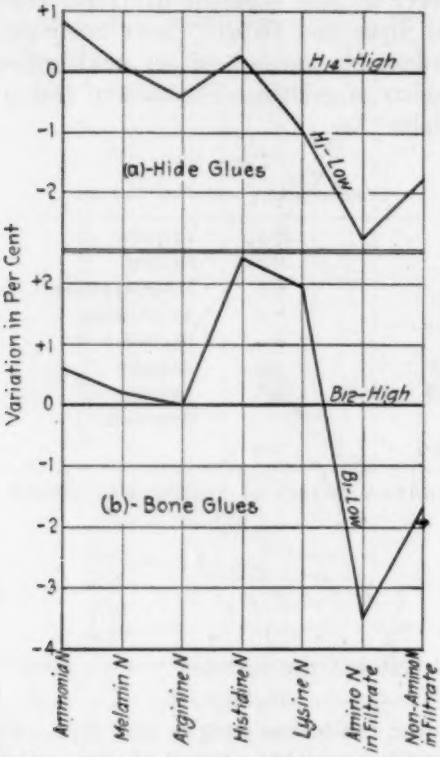
assuming that the molecular weight was 839. This value was obtained by a mathematical treatment of the equilibrium existing in a gelatin-acid system, assuming the gelatin to be a diacid base. By assuming the gelatin to be monoacid, Wilson [33] found a molecular weight of 768, and wrote the formula:

$$C_{32}H_{52}O_{12}N_{10}.$$

[29] Fischer, Levene and Anders: *Z. physiol. Chem.*, **35** (1902), 70.
[30] H. D. Dakin: *J. Biol. Chem.*, **44** (1920), 524.
[31] D. D. Van Slyke and A. Hiller: *Proc. Nat. Acad. Sci.*, **7** (1921), 185.
[32] H. R. Procter: *J. Chem. Soc.*, **105** (1914), 313.
[33] J. A. Wilson: *J. Am. Leather Chemists' Assoc.*, **12** (1917), 115.

The method of examining proteins suggested by Van Slyke [34] has been applied to gelatin by Van Slyke and to a large number of gelatins and glues by the writer.[35] Some relations of importance have been observed. In the first place there is a distinct variation observed on passing from the high to the low-grade product.

FIG. 11.



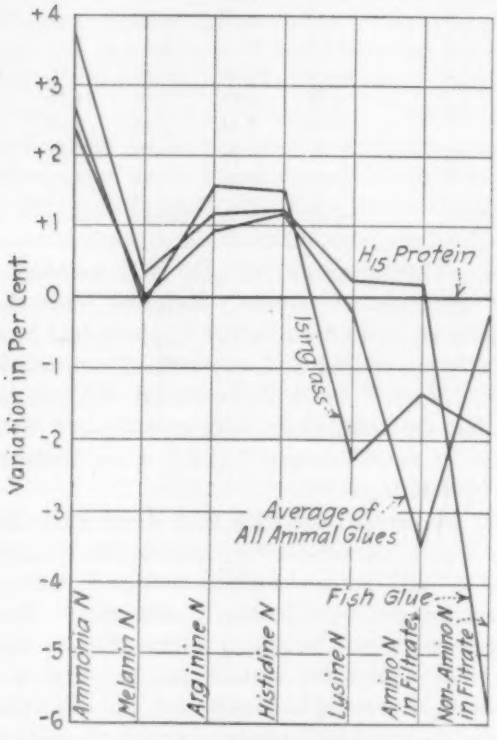
Variation in amino-acid constitution of high and low grade hide and bone glues.

This is seen in Fig. 11. And practically the same type of variation is observed on comparing the bone with the hide glues. The low grades, and the bone glues, have the higher ammonia, histidine and lysine content, and the lower arginine, amino, and non-amino nitrogen of the filtrate. The latter two groups contain practically all of the mono-amino acids.

[34] D. D. Van Slyke: *J. Biol. Chem.*, 10 (1911), 15; 22 (1915), 281.
[35] R. H. Bogue: *Chem. Met. Eng.*, 23 (1920), 154.

The explanation given to account for these differences is that as the cooking of the stock progresses, and higher temperatures and longer periods of heating are employed, more and more of the non-collagenous proteins become hydrolyzed. True collagen

FIG. 12.



Varation in amino-acid constitution of different products.

is easily converted into gelatin, but more drastic treatment is required for the hydrolysis of the more resistent proteins. These include keratin, elastin, mucin, and chondrigin. The amino-acid composition of these is different from that of gelatin, and so becomes manifest upon the examination described above.

Fish glues and isinglass were also studied and were found to give higher arginine and histidine and lower proline and oxyproline portions than any other types. This is shown in Fig. 12.

The following table shows some of the data:

TABLE VI.

Distribution of Nitrogen in Gelatins and Glues.

	Gelatin (Van Slyke)	Gelatin	Average Hide Glues	Average Bone Glues	Isinglass	Fish Glues
Ammonia N	2.25	1.33	2.90	4.55	3.98	5.15
Melanine N	0.7	0.78	0.59	0.91	0.68	1.12
Cystine N	0?	0	0	0	0	trace
Arginine N	14.70	12.61	13.90	13.17	14.20	13.80
Histidine N	4.48	0.82	2.19	1.78	2.33	2.04
Lysine N	6.32	8.34	7.97	8.28	6.06	8.58
Amino N of filtrate	56.3	60.00	56.89	26.27	28.65	60.20
Non-amino N of filtrate...	14.9	15.49	15.63	15.25	13.59	9.66
Total regained	99.02	99.37	100.02	100.21	99.49	100.55

Structure.—The structure of gels is a problem which has occupied the attention of physical chemists since the inception of colloid chemistry, and even before Graham had introduced the distinction between colloid and crystalloid. Frankenheim [36] in 1835 and von Nägeli [37] in 1858 concluded that jellies were two-phased and that the solid phase was crystalline. This view has been supported by von Weimarn [38] and Levites,[39] and is at present championed by Bradford.[40]

Bütschli [41] introduced the idea that there were definite pores in a jelly, and van Bemmelen [42] extended this conception to the postulation of a "cell-like structure of definite form . . . hanging together at certain points, forming a network." This idea of a network structure in gels has been adhered to by many investigators, but from somewhat variant points of view. Hardy [43] concludes from a microscopical study that the solid phase consists of a solid solution of water in gelatin, and the liquid phase a solu-

[36] Frankenheim: "Die Lehre von der Kohäsion," Breslau, 1835.

[37] v. Nägeli: "Pflanzenphysiologischen Untersuchungen," Zurich, 1858.

[38] v. Weimarn: *Kolloid-Z.*, **2** (1908), 76, 230, 275, 301, 326.

[39] Levites: *Ibid.*, **2** (1908), 161, 273.

[40] Bradford: "The Physics and Chemistry of Colloids, and Their Bearing on Industrial Questions," Report of a General Discussion by The Faraday and Physical Societies of London, October 25, 1920. H. M. Stationery Office, 1921, p. 44.

[41] Bütschli: "Untersuchungen über Structuren," Leipzig, 1898.

[42] v. Bemmelen: *Z. anor. Chem.*, **18** (1898), 14.

[43] Hardy: *Proc. Roy. Soc.*, **66** (1900), 95.

tion of gelatin in water, and that gelation consists in the separation of the sol into a solid open framework with an interstitial fluid phase. This idea is accepted by Freundlich [44] and Anderson,[45] and in essential respects by Miss Lloyd [46] and Fischer.[47] Wo. Ostwald [48] injected the conception of a two-phase liquid-liquid system, and Bancroft [49] has adhered to this idea.

Procter [50] has discarded the two-phase theory of gel structure and postulated the existence of a solid solution of the exterior liquid in the colloid in which both constituents are within the range of the molecular attractions of the mass. This theory was the result of his findings that in a gelatin acid water system equilibrium resulted from the combination of the gelatin and acid to form easily dissociated salts, and that the osmotic pressure of these salts and the Donnan Equilibrium determined the volume of a swollen jelly. Loeb [51] has carried the idea of Procter to a further explanation of colloidal behavior as described later.

These three schools of thought upon colloid structure represent the present status of the problem. For purposes of classification, although not strictly correct, they may be referred to as the crystalline theory, the colloid theory, and the molecular theory respectively.

The concept of a crystalline structure in gels has been studied by Scherrer,[52] who has made many examinations of gels by means of the Röntgen photograph. He found that certain rigid gels as silicic and stannic acids exhibited well-marked crystalline interference figures in addition to the characteristics of amorphous substances, but in the gel of gelatin the crystalline interference figures were entirely lacking. These different types of gels possess other characteristic dissimilarities. The gel of silicic acid, for example, develops, on drying, pores that are filled with air, and which may be filled by imbibition with a liquid other than the

[44] Freundlich: "Kapillarchemie," Leipzig, 1909.
[45] Anderson: *Z. physik. Chem.*, **88** (1914), 191.
[46] D. J. Lloyd: *Biochem. J.*, **14** (1920), 147.
[47] Martin Fischer: "Soaps and Proteins," New York, 1921.
[48] Wo. Ostwald: *Arch. ges. Physiol.*, **109** (1905), 277; **111** (1906), 581.
[49] W. D. Bancroft: "Applied Colloid Chemistry," New York (1921), 239, 242.
[50] H. R. Procter: *J. Chem. Soc.*, **105** (1914), 313.
[51] Jacques Loeb: *J. Gen. Physiol.*, **3** (1921), 827; **4** (1921–22), 73, 97, 351.
[52] P. Scherrer: *Nachr. Kgl. Ges. Wiss. Göttingen* (1918), 96.

original solvent. The elastic gels such as gelatin do not develop such pores, and the dried gel will not imbibe a foreign liquid, as, for example, benzene. Harrison [53] has even succeeded in obtaining spherical coagulation-forms of starch which strongly resemble the so-called spherites that were obtained by Bradford from gelatin, but these are not regarded as crystalline.

The theory of Procter, while explaining adequately the swelling phenomena of gelatin, does not account for other colloidal behavior, as viscosity fluctuations with time, syneresis, or the process of gelation itself.

The net structure hypothesis meets with a number of objections. Of not least importance is the failure of its proponents to account for the existence of such a structure. In the sol form, they say, the structure does not exist; in the gel form it does exist. What has brought about the change and why was it produced? The sudden appearance of structure must be accounted for.

Again, they affirm by this theory that the jelly consists of a sponge-like or honeycomb structure consisting of gelatin as a continuous solid or semi-solid phase, and water (containing inorganic ions and some gelatin molecules in solution) as the dispersed phase. If this were true it should not be difficult to extract the water by moderate pressures, but this cannot be done. Reinke [54] has pointed out that at a pressure of 41 atmospheres the gel of *Lamineria* increases in volume by the absorption of water 16 per cent., and at one atmosphere 330 per cent. Posnjak [55] has shown that at 377 cm. of mercury gelatin gel increases in volume nearly 100 per cent., while at 38 cm. the increase is over 250 per cent. Quincke [56] and Hatschek [57] have shown that a volume contraction accompanies the swelling of gelatin to the extent of nearly two per cent., and Widemann and Ludeking [58] have reported that 5.7 gram-calories of heat are liberated by the swelling of one gram of gelatin. These facts are not explained

[53] N. Harrison: *J. Soc. Dyers and Cols.*, **32** (1916), 32.

[54] Described by Hatschek: "Introduction to the Physics and Chemistry of Colloids," London, 1913, 56.

[55] Posnjak: *Kolloidchem. Beihefte*, **3** (1912), 417.

[56] Quincke: *Arch. ges. Physiol.*, **3** (1870), 332.

[57] Hatschek: *Lib. cit.*, 55.

[58] Widemann and Ludeking: *Ann. Physik.*, N. F. **25** (1885), 145.

by the assumption that gelatin swells, like a sponge, by the imbibition of water into the porous structure of the gel.

It should also be urged that diffusion and conductivity take place primarily through the continuous phase and not the dispersed phase of a gel, and if the development of the structure in the gel necessitates the assumption of a reversal of phase, as assumed by Fischer [59] and others, it is difficult to understand the nearly identical degrees of diffusion and of conductivity exhibited by the sol and the gel forms, as pointed out by Graham [60] and by Arrhenius [61] respectively.

It appeared to the writer of the highest importance to a complete understanding of the structure of gels that the sols should be studied also, and that the several conditions affecting the change from the one into the other be clearly defined. This equilibrium was investigated by two series of experiments.[62]

(To be Concluded.)

The Forced Convection of Heat from a Pair of Fine-heated Wires. J. S. G. THOMAS. (*Phil. Mag.*, February, 1922.)—A form of anemometer is in course of development in London in which a pair of electrically heated, parallel wires are immersed in the stream of gas. The velocity of flow is deduced from the change of temperature or consequent change of resistance caused by the motion of the gas. The present paper displays some interesting results in this connection. When the wires, placed perpendicular to the direction of flow and in a plane containing the axis of the pipe and traversed by fixed currents, were kept separated by a certain range of distances, then the resistance of the down-stream wire first fell as the speed of flow increased, then rose again to its value with the gas, air in this case, at rest, passed beyond the original value, reached a maximum, sank to the original value once more, and after this continued to sink, no matter how much the velocity was increased. There were thus two different speeds at which the resistance of the wire had the same value as with the gas at rest. With a different interval between the wires there was but one such speed and with still a different interval no similar speed existed at all. The temperature of the down-stream wire is determined by the loss of heat due to the stream of air and to the heat carried to it from the other wire. Of course eddies in the gas contribute their effect also.

G. F. S.

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[59] Martin Fischer: *Loc cit.*

[60] Thomas Graham: *Cit. sup.*

[61] S. Arrhenius: *Cit. sup.*

[62] R. H. Bogue: "The Sol-Gel Equilibrium in Protein Systems," and "The Structure of Elastic Gels," *J. Am. Chem. Soc.*, on press.

Observations and Experiments on the Occurrence of Spark Lines. G. A. HEMSALECH and A. DE GRAMONT. (*Phil. Mag.*, February, 1922.)—Years ago Sir Norman Lockyer noticed that certain spectrum lines not produced at all in the flame and appearing only feebly in the arc sprang into brightness when a strong condenser spark was made the source of light. Such lines are known as "enhanced" or "spark" lines. Under certain conditions spark lines have been seen in the inner cone of the gas flame. There has been, moreover, much uncertainty as to their origin. They have been ascribed to high temperature, to electro-luminescence and to ionic collision. After the present investigators have developed a simple method of getting arc spectra with such metals as tin and lead, they find that lowering the ionization of the arc by blowing air through it causes the spark lines to appear. These lines, however, disappear when the cathode is white-hot carbon. "They are brought out prominently, on the other hand, when the electrodes are cooled down to −190° C. by immersion in liquid air." "The whole of our experiment points to the fact that spark lines are emitted when electric currents are passed through media (vapours or gases) which possess a low degree of ionization. Since such a process involves the application of powerful electric forces giving rise to the establishment of high-potential gradients in the medium concerned, we are finally lead to conclude that the emission of spark lines is connected with the existence of strong electric fields. A simple consideration shows indeed that for small pole distances the electric field within the arc-gap can be very great even with a small potential difference. Thus, for a pole distance of 0.05 mm. the intensity of the electric field with an applied potential 110 volts is equal to 22,000 volts per cm. As we have shown in the course of this research spark lines are strongly emitted by the arc only while the distance between the electrodes is precisely very small." G. F. S.

Surface Tension of Soap Solutions for Different Concentrations. A. L. NARAYAN and G. SUBRAHMANYAM. (*Phil. Mag.*, April, 1922.)—Marangani drew the conclusion from the rise of soap solutions in capillary tubes that the surface tension is for wide ranges of concentration independent of the strength of the solution. White and Marden, on the other hand, have given out as a result of their experiments that the surface tension does change with concentration in the ratio of 2 to 1 or even more. The present investigators used two methods, ascent in capillary tubes and measurement of the excess of pressure within a soap bubble. They have established by the agreement of both methods that the surface tension has the same value for a saturated solution and for all solutions down to those containing only 2 or 3 per cent. as much soap as the saturated solution. For very dilute solutions, however, the surface tension grows larger, beginning when there is .23 g. of soap per 100 c.c. of solution.

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THERMAL STRESSES IN CHILLED IRON CAR WHEELS.[1]

By G. K. Burgess and R. W. Woodward.

[ABSTRACT.]

For over half a century most of the freight cars in this country have been equipped with chilled iron car wheels. These wheels have given general satisfaction, even under the present existing conditions of greater speeds and increased stresses due to the use of heavier wheel loads. It has been observed, however, that failures of chilled iron wheels occur occasionally at the foot of long, steep grades, and the greatest cause of such failures appears to be the heating of the tread by the prolonged application of the brake shoe.

The difference in temperature between the tread and the hub induces stresses in the wheel, which in some cases are sufficient to cause cracking and failure, possibly resulting in the derailment of the car under which the wheel is placed. A conception of the seriousness of this type of failure may be obtained from the report of one of the large railroad systems wherein it is indicated that during a test covering a period of approximately seven months, about 19 per cent. of the chilled iron wheel failures occurred in the plate, which is the type of failure resulting from thermal stresses.

A method was developed at the Bureau of Standards for testing car wheels in the laboratory under conditions approximating severe service. The wheels were heated by passing an electric current through a band of iron encircling the wheel; the resulting stresses were calculated from strain gage measurements after correcting for thermal expansion.

Twenty-eight wheels of varying weights and design from three manufacturers were tested in this manner, of which sixteen failed by cracking in the plate. Although the total number of wheels tested is too small to draw any definite conclusions, the results seem to point to the following generalities which should be confirmed by a greater number of tests:

1. The maximum stresses developed are very close to the

* Communicated by the Director.

[1] Technologic Paper, No. 209.

tensile strength of the cast iron and are some function of the strength of the iron.

2. The maximum tensile stresses occur in a radial direction near the junction of the double plates in the M.C.B. or Washburn type of wheel. In the arch plate type the maximum stress is somewhat nearer the hub. This seems a desirable condition in that it lies in the region where it is counteracted by the strains due to forcing the wheel on to its axle.

3. The stress in a tangential direction on the outer face and also the stress in both the radial and tangential directions on the bracket side of the wheel are relatively small when compared with those in a radial direction on the outer face of the wheel.

4. By proper distribution of metal in the single plate type of wheel there would appear to be a possibility of securing a wheel more capable of meeting service requirements.

5. With identical rates of heat input the heavier weight wheels withstand the effect of tread heating with less strain than the lighter wheels.

6. The tests also lead one to believe that the operating conditions to which wheels are subjected may be as important a factor in the safety of the wheel as are the problems arising in their manufacture.

INTERFERENCE METHODS FOR STANDARDIZING AND TESTING PRECISION GAGE BLOCKS.[3]

By C. G. Peters and H. S. Boyd.

[ABSTRACT.]

PRECISION gages, which are blocks of metal (usually steel), having two opposite faces plane, parallel, and a specified distance apart, are used in the shop as reference end standards for checking micrometers and other measuring instruments, and also as distance pieces or size blocks for precise mechanical work. The extensive use of precision gages necessitated by the small tolerances allowed in the manufacture of interchangeable machine parts has required more accurately determined end standards and more rapid and precise methods for comparing gages with these standards than have been previously available.

Since comparisons of end standards with line standards by means of micrometer-microscopes and of precision gages with end

[3] Scientific Papers, No. 436.

standards by means of contact instruments are subject to appreciable errors, methods which make use of the interference of light waves were used in making these measurements. With the interference methods described in this article, the planeness and parallelism errors of precision surfaces can be measured, and the length of standard gages can be determined by direct comparison with the standard light waves with an uncertainty of not more than a few millionths of an inch. The errors of other gages can be determined by comparison with these calibrated standards with equal precision. This process makes the standard light waves, which have been determined to 1 part in 4 or 5 million relative to the international meter, the standards of length for this work.

The apparatus used for calibrating standards and comparing other gages with these standards is illustrated by line drawings and thoroughly explained.

ELECTROMOTIVE FORCE OF CELLS AT LOW TEMPERATURES.[3]

By G. W. Vinal and F. W. Altrup.

[ABSTRACT.]

THE practical importance of a knowledge of the electromotive behavior of dry cells and storage batteries at low temperatures has arisen from their use in the Arctics and at high altitudes. Measurements on dry cells and storage batteries cooled to —72° C. by carbon dioxide snow and to —170° C. by the use of liquid air were made. The Gibbs-Helmholtz equation was applied to the observations, and excellent agreement between theory and observation was found. At the lowest temperatures high values of voltage were sometimes observed, and the polarity was often reversed. A possible explanation based on the Nernst equation is given.

CONSTRUCTION AND OPERATION OF A SIMPLE HOME-MADE RADIO RECEIVING OUTFIT.[4]

[ABSTRACT.]

THE apparatus used for the reception of radio messages may be a home-made affair, very simple and inexpensive, or it may be elaborate and expensive. All that is necessary for receiving radio

[3] Scientific Papers, No. 434.
[4] Circular No. 120.

messages is a device for collecting power from incoming radio waves, a suitable circuit " adjusted " or " tuned " electrically to the frequency of the incoming waves, and apparatus for changing the received power into audible sounds.

This Circular describes the method of constructing in the home a very simple and inexpensive receiving outfit from materials which can be easily secured. The cost of the materials need not exceed $10. Satisfactory results have been obtained from sets constructed according to these instructions by persons having no previous experience with radio.

The preparation of this publication had its origin in work undertaken by the Bureau of Standards, in coöperation with the Bureau of Markets and Crop Estimates of the Department of Agriculture, in connection with the broadcasting by radio of Government news and information. This broadcasting service has proved to be very useful to farmers, bankers, dealers, and many others, and a considerable demand arose for information regarding simple receiving equipment.

The five essential parts of a radio receiving station are the antenna, lightning switch, ground connection, receiving set, and telephone receivers. The antenna is the device for collecting power from the incoming waves. The signals received on the antenna are converted into an electric current in the receiving set, and a corresponding sound is produced in the telephone receivers.

The antenna may be a wire about 75 feet long, attached through insulators to buildings or other convenient supports.

The lightning switch protects the receiving set from damage by lightning. It may consist simply of a small single-pole, double-throw battery switch. The lightning switch connects the antenna directly to ground when the receiving station is not in use. When the antenna and connection to the ground are properly made and the lightning switch is closed, the antenna acts as a lightning rod and is a protection to the building.

The principal part of the station is the " receiving set." The outfit described in this Circular consists of two parts, the " tuning coil " and the " crystal detector," and in more complicated sets still other elements are added.

The " tuning coil " consists of a coil of wire which may be wound on a cylindrical cardboard tube such as an oatmeal box. The coil of wire is attached at a number of points, from which

connections are made to the points of a multiple-point switch. The adjustment or "tuning" of the receiving set to the frequency or wave-length of the incoming waves is made by adjusting the position of the switch handle so that connection is made with varying numbers of turns to the tuning coil.

The crystal detector consists of a small piece of selected galena or other tested mineral, with suitable mounting.

The tuning coil, switch, and crystal detector are mounted on a wooden base.

The telephone receiver must be purchased. A single telephone receiver may be used, but a pair will give better results.

The outfit described in this Circular will enable anyone to hear radio code messages or music and voices sent from a medium power transmitting station within an area about the size of a large city, and from high power stations within 50 miles, provided that the waves used by the sending stations have a wave frequency between 500 and 1500 kilocycles per second (that is, wave-lengths between 600 and 200 metres). This equipment will not receive uninterrupted continuous waves. Occasionally, much greater distances can be covered, especially at night. Sets constructed according to these instructions have given clear reception of music transmitted by radio telephone from stations 300 miles distant.

AN IMPROVED METHOD FOR PREPARING RAFFINOSE.[5]

By E. Clark.

[ABSTRACT.]

FIVE kilograms of coarsely ground cottonseed meal are thoroughly moistened with two litres of water and allowed to stand over night. It is then loosely packed in a cylindrical percolator, and sufficient water added to saturate the meal and leave a stratum above it. When the liquid begins to run from the percolator, more menstrum is added, from time to time, until a sample of the percolate after defecation with dry basic lead acetate, has an optical rotation of not more than 1° in a 2 dm. tube.[6] The process is then

[5] Scientific Paper, No. 432.

[6] As there are substances in the meal which are extracted much more slowly than the sugar, and which cause difficulty in the subsequent steps as well as give an inferior product, it is essential to obtain a quite rapid percolation, consuming not more than 30 to 35 minutes; it is not expedient to carry the extraction beyond where the optical rotation of the liquid is less than 1° in a 2 dm. tube.

stopped, and the percolate is treated with a solution of basic lead acetate until no more precipitate is formed. The yellow precipitate is filtered off upon large folded filters and finally washed on the filter with a little water. The filtrate and washings are freed from the excess of lead with oxalic acid. The filtrate from the lead oxalate is measured, and the optical activity of the liquid determined. It is then made distinctly alkaline to litmus with sodium hydroxide. The precipitate thus formed flocks out and settles to the bottom of the vessel in a few minutes. The supernatant liquid is next filtered through a Buchner funnel provided with a thin layer of decolorizing carbon on filter paper. When all has passed through, the precipitate is placed on the filter and drained.

The raffinose is next removed from the solution by forming the insoluble calcium raffinosate. To conveniently accomplish this the liquor is cooled to 10° C. or lower, placed in a suitable container, and rapidly stirred with a mechanical stirring device. As it is being agitated a quantity of powdered active lime, preferably 200 mesh, but not coarser than 100 mesh, sufficient to precipitate all the sugar is slowly sifted in. After all has been added, the stirring is continued for about five minutes. If the lime is active and the optical activity of the solution is calculated to raffinose hydrate with a specific rotation of about 105°, 1 gram of lime to 1 gram of raffinose is sufficient for complete precipitation. However, unless the activity of the lime is known, it is advisable to test the liquid to see if all the sugar has been removed; if not, more lime should be added. The calcium raffinosate is filtered off, washed by grinding up to a smooth paste with 2½ litres of cold lime water, and again filtered.

It is next carbonated to neutrality. The device illustrated in the article was used for this purpose. The cake of raffinosate is placed in a deep, narrow can of about 8 litres capacity and filled three-fourths full of water at 50° C., and a lively stream of carbon dioxide is passed through the apparatus while it is being turned about 1500 r.p.m. In this way the lime is neutralized in 4 or 5 minutes without any loss of CO_2. The solution is filtered while hot, and the precipitate is washed by grinding up with two litres of water and again filtering. The combined liquors are evaporated under diminished pressure to 70 to 75 per cent. total solids and warmed to about 60° C. To this syrup 95 per cent. ethyl alcohol is

added just to saturation. The alcoholic solution is then warmed on the water bath to about 60° C. and filtered through a small Buchner funnel in which has been placed a mat of washed asbestos. The filtrate is seeded and placed in the ice box to crystallize.

The raffinose is filtered off from the mother liquor, washed first with 80 per cent., then 95 per cent. alcohol, and dried. The yield is from 2.3 to 4 per cent. of raffinose, depending upon the meal used. The crude sugar thus prepared is quite pure, containing only from 0.06 to 0.08 per cent. ash.

To purify crude raffinose a 40 per cent. solution (anhydrous sugar) is made by dissolving it in distilled water at 70° C. The warm solution is filtered through a mat of asbestos and placed in the ice box to crystallize. The crystals are freed from mother liquor, washed with 80 per cent., then 95 per cent. alcohol, and dried.

An alternative method of recrystallization is to concentrate the above 40 per cent. solution under reduced pressure to 70 per cent. total solids, warm to 70° C., and add two volumes of 95 per cent. alcohol with constant stirring. Crystallization begins almost at once and is complete in a few hours. The crystals are filtered off, washed with 95 per cent. alcohol, and dried.

Fluorescence and Photo-chemistry. R. W. WOOD. (*Phil. Mag.*, April, 1922.)—"Though it has been known for some time that many fluorescent solutions are bleached by the action of light, Perrin appears to have been the first to definitely associate fluorescence with chemical change and to regard the light emitted by fluorescent substances as due to the 'flashes' of exploding molecules." At his summer laboratory, East Hampton, Long Island, in 1919 and 1920, Professor Wood subjected sundry fluorescent solutions to a beam of sunlight concentrated by a lens of short focus and 6 inches in diameter. He thus got sufficient quantities of the products resulting from the action of light to enable him to examine their optical and chemical properties. "Usually the decomposition of the fluorescent substance by the action of light yields a colored non-fluorescent substance which is bleached by the further action of light to a colorless solution." Photographs were made of the absorption spectra of the original solutions and of the solutions after the action of light. "Fluorescein (uranine), for example, which is lemon-yellow by transmitted light, is changed into a non-fluorescent compound (photofluorescein), which is orange-red, with an absorption band of a totally different form." "The time required to effect the change varies with the nature of the substance: eosine is completely changed in two or three minutes, while rhodamine in the same concentration

requires several hours." The effect of light on rhodamine varies with the solvent. In aqueous solution a bleaching effect takes place without the formation of an intermediate colored body, but in alcoholic solution such an intermediate body is developed which fluoresces with green light, whereas the rhodamine has orange-red fluorescence. Certain specimens of rhodamine almost cease to fluoresce at 100° C., while eosine manifests no temperature effect.

Careful experiments showed that, at least in the case of fluorescein, the intensity of the fluorescent light is directly proportional to the intensity of the exciting light.

The Johns Hopkins physicist sought to test Perrin's hypothesis that fluorescence is due to molecular disintegration. There are two cases in which fluorescent substances do not fluoresce when exposed to light: *a* in general when in too concentrated solutions, *b* in particular when certain specimens of rhodamine are heated. A strong solution of eosine was put in concentrated sunlight. It showed no trace of fluorescing nor did it suffer any change by its exposure to light, while a dilute solution both emitted fluorescent light and underwent change. These results tend to show that fluorescence and chemical change are parallel processes. Next two similar solutions of rhodamine were exposed to light equally, but one was kept at 100° C. The cold solution emitted much brighter fluorescent light than the other, yet decomposition was equal in the two solutions. Thus the outcome of the two experiments is contradictory. The first favors Perrin's views. The second seems to negative them.

The change produced in fluorescent solutions is not in proportion to the energy absorbed from the incident light. Light of great intensity acting for a short time produces more change than a weaker light acting for an equivalently longer time.

The announcement is made that for future experiments a mirror is available having a 32-inch aperture and focal length of 18 inches, which produces so intense a concentration of sunlight as to melt platinum foil instantly. G. F. S.

Potash as a By-product in the Blast Furnace Industry.—WILLIAM H. ROSS and ALBERT R. MERZ, of the United States Bureau of Soils (*Jour. Ind. Eng. Chem.*, 1922, xiv, 302–303), report a study of the potash content of iron ore, limestone, coke, and blast furnace slag. The potash content of iron ore ranged from 0.05 per cent. to over 2 per cent., the average content was 0.19 per cent. The average potash content of limestone was 0.20 per cent., of coke 0.24 per cent. and of slag 0.56 per cent. In the blast furnace, 5.6 pounds of potash (K_2O) are lost by volatilization for each short ton of pig iron produced. During the year 1920, it is estimated, 115,000 short tons of potash were lost in this manner. In order to recover this potash, a dry system of purification of the furnace gases will be necessary. The collected dust would be of value as a source of potash, especially in case of an emergency. J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

THE USE OF ARTIFICIAL ILLUMINANTS IN MOTION PICTURE STUDIOS.[1]

By L. A. Jones.

THE paper deals with the effects of various artificial and natural illuminants upon the photographic material and also with the action of these light sources upon the retina of the eye. In the introductory portion, some space is devoted to a discussion of the nomenclature and terminology used in dealing with the subject matter. The well-known photometric terms are defined and classified and several photographic units parallel in meaning to the photometric units are defined. The new terms defined in this paper are "photic flux," "photoibility," "photocity," "photic efficiency," and "photon." The last word is proposed as a name for the unit of photic flux and is defined as a photographic equivalent of the lumen. Some space is devoted to the relative photographic and visual efficiency of various artificial illuminants and several tables of data relating to the subject are given. The transmission characteristics of photographic lenses are treated and quantitative data relative to this are given. A method of calculating the illumination required in the studio in order to obtain satisfactory exposures with photographic materials of known characteristics is outlined.

THE GLOSS CHARACTERISTICS OF PHOTOGRAPHIC PAPERS.[2]

By L. A. Jones and M. F. Fillius.

AT the present time the gloss characteristics of photographic papers are designated by such more or less vague terms as "matte," "semi-matte," "velvet," etc. The desirability of expressing this

* Communicated by the Director.

[1] Communication No. 135 from the Research Laboratory, Eastman Kodak Company, and published in *Trans. Soc. Mot. Pic. Eng.*, No. 13, p. 74.

[2] Communication No. 134 from the Research Laboratory, Eastman Kodak Company, and published in *Jour. Opt. Soc. Amer.*, March, 1922, p. 140.

factor more precisely in numerical terms is pointed out. A method of defining gloss in terms of the relative intensity of diffusely and regularly reflected light is outlined. The goniophotometer, an instrument for measuring the distribution of the light reflected from a surface, is described and the method of computing the gloss of the surface from the readings obtained is outlined. The determination of gloss by this method requires two measurements of the brightness of the surface at different angles. In order to eliminate the errors inherent in such a method, a special instrument called a " gloss meter " was designed and constructed whereby the gloss of any surface may be determined by a single reading. This instrument is described. Gloss measurements on a large number of developing-out papers are given, and the effect upon gloss of various surface treatments of the raw stock is determined. From an analysis of the readings obtained, a tentative numerical definition of the words matte, semi-matte, semi-gloss and glossy in numerical terms is given.

Action of Fuming Sulphuric Acid on Cast Iron and High Silicon Iron.—Apparatus, which is made of cast iron or high silicon iron and is used for the handling of fuming sulphuric acid, frequently cracks from no apparent cause. Heavy pipes, not subjected to any unusual strain, may crack longitudinally with a loud report. T. F. BANIGAN (*Jour. Ind. Eng. Chem.*, 1922, xiv, 323) has studied the prolonged action of fuming sulphuric acid, known as oleum or 103.37 per cent. sulphuric acid, on a high silicon iron alloy, on amorphous silicon, and on silicon carbide. Both the alloy and the silicon were attacked at room temperature with the production of silicon dioxide. The silicon carbide was not attacked even at a temperature of 100° C. Amorphous silicon was not attacked by 96 per cent. sulphuric acid acting for one week at a temperature of 100° C. Hence the sulphur trioxide in the fuming acid readily oxidizes silicon, either free or alloyed with iron. High silicon alloys are rapidly corroded by the fuming acid since the silicon is oxidized to voluminous silica (silicon dioxide), and a fresh surface is continually exposed. In cast iron and malleable iron, the sulphur trioxide penetrates the pores, oxidizes the silicon, and produces silica which occupies a larger volume than did the silicon from which it was derived. An internal strain is thereby created, and gives rise to failure of the apparatus. Apparently neither the silicon carbide nor the carbon in the casting has any action on the acid or any responsibility for the failure of the apparatus. J. S. H.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

POISONOUS METALS ON SPRAYED FRUITS AND VEGETABLES.[1]

By W. D. Lynch, C. C. McDonnell, J. K. Haywood, A. L. Quaintance, and M. B. Waite.

[ABSTRACT.]

THE amounts of arsenic, lead and copper remaining on mature fruits and vegetables which have been sprayed according to various schedules were determined in the Bureau of Chemistry.

Because of overspraying or late spraying, comparatively large quantities of spray residues were found in some cases. This emphasizes the importance of spraying according to the schedules recommended by the Bureaus of Entomology and Plant Industry.

The extent of the reduction of spray residues on the mature fruit and vegetables by washing and wiping them was determined by a series of analyses before and after such treatment.

When peeled, sprayed fruits and vegetables contain essentially the same amounts of arsenic, lead, and copper as the unsprayed products, indicating that practically all of the spray residues can be removed by peeling.

When fruits and vegetables are sprayed in accordance with the schedules recommended by the Bureaus of Entomology and Plant Industry, but little of the material used remains on the fruit or vegetable at harvest time.

DOMESTIC AND IMPORTED VERATRUM (HELLEBORE), *VERATRUM VIRIDE* AIT., *VERATRUM CALIFORNICUM* DURAND, AND *VERATRUM ALBUM* L.[2]

By Arno Viehoever, George L. Keenan, and Joseph F. Clevenger.

[ABSTRACT.]

MEANS for the differentiation of the rhizomes and roots of domestic Veratrum (*Veratrum viride*), imported Veratrum (*Veratrum album*), and *Veratrum californicum*, a form hitherto not studied histologically, have been devised.

* Communicated by the Acting Chief of the Bureau.

[1] *U. S. Department of Agriculture Bulletin 1027*, issued April 17, 1922.

[2] Published in *J. Am. Pharm. Assoc.*, 10 (1921): 581; 11 (1922): 166.

Botanical.—The endodermal cells, forming a sheath in the rhizome and root, the cells of which show different thickenings of the inner tangential and radial walls, are the main differentiating characteristics. The calcium oxalate raphide bundles occurring in both rhizome and root, differing in length in the different species, were found to be more or less characteristic. Calcium oxalate raphides in the leaf scales attached to the rhizomes of *Veratrum viride* and *Veratrum album* are longer than those in the rhizomes and roots of these species. The epidermal cells of the roots also differ in size, being smallest in the case of *Veratrum viride,* larger in *V. album,* and still larger in *V. californicum.* These characteristics vary greatly, showing a tendency to overlap in some instances.

Chemical.—The alkaloids of *Veratrum album* do not differ much from those of *Veratrum viride.* The alkaloid content in both species varies within the same limits, so that no differentiation of species is possible on this basis. Microsublimation indicates close chemical relationship, but does not permit of ready differentiation. The close botanical and chemical relationship of *Veratrum viride* and *Veratrum album* justifies the adoption of the same standards for the medicinal material obtained from both species. The standards suggested for the medicinal drugs are at least 1 per cent. for alkaloids and not more than 8 per cent. total nor more than 4 per cent. acid-insoluble ash.

General.—The present market quotations indicate that *Veratrum album* and *Veratrum viride* are considered of equal value. No data, however, as to the relative value of *Veratrum viride* and *Veratrum album,* definitely identified as such, appear to be available. The means pointed out for their histological differentiation should make possible comparative studies of the plants as found in the market. Their relative values as therapeutic agents and as insecticides may be thus established.

FAKE SAFFRON.[1]

By Arno Viehoever and J. F. Clevenger.

[ABSTRACT.]

THE appearance of some material imported from Spain was skillfully changed, so that it might pass for saffron. It resembled Crocus in appearance and in flavor. Close inspection, however, showed that instead of the stigmas characteristic of Crocus, tubular

[1] Published in *J. Am. Pharm. Assoc.,* 10 (1921): 671.

florets characteristic of a number of the Compositæ were present. This substitution was complete, no stigmas of Crocus being present.

The substitute was identified as a species of *Onopordon* closely related to *Onopordon sibthorpianum* Boiss and Heldr. The materials had been dyed with a mixture of Tartrazine and commercial Ponceau 3 R. It was weighted with a mixture of at least 5 per cent. potassium nitrate and borax. About 4 per cent. glycerin was also present. The material was evidently flavored with saffron oil.

Corrosion of Iron and Steel.—This important subject has been extensively studied, and the present state of opinion with a summary of much of the literature was presented in a communication by A. Pickworth, M.Sc., to the North-east Coast Institution of Engineers and Shipbuilders (Newcastle-upon-Tyne). Attention is called to the great waste that such corrosion involves and to the several theories of causes that have been proposed. It appears that iron does not rust in water containing only oxygen, but the presence of some substance giving rise to ionized hydrogen is required. Under ordinary conditions the active substance is carbonic acid, but, of course, other acids may be present, especially those produced by the oxidation of the organic matters of soil. The air of built-up areas is almost always contaminated with sulphur acids, and iron rust in such places usually contains notable amounts of sulphates. Electric conditions have an important bearing on corrosion. A difference of potential of the area exposed to water will determine the development of oxidation at certain points. Doctor Friend has recently investigated the subject with much care and offers a somewhat new theory. The oxidation of iron in contact with liquid water is catalytically accelerated by the ferric hydroxide hydrosol being alternately reduced by contact with the iron and oxidized again by contact with atmospheric oxygen.

Iron, in any of its forms, is attacked by a weak solution of carbonic acid, forming ferrous carbonate, which in the presence of free oxygen is converted into ferric hydroxide, thus again liberating carbon dioxide, which reforms the acid condition with the water, capable of repeating the process. It is evident that the small amount of carbonic acid normally in water may carry on the oxidation continually. Some years ago, a process for water purification was based on this principle. Ferric hydroxide has a high adsorptive power for organic matters, but is active only in the fresh colloidal state. By agitating water with iron scrap, fairly free from oil and rust, a green turbidity appears which soon changes to red. If now the water is filtered, a great deal of the organic matter will be held by the ferric hydroxide, which, of course, will be retained on the filter.

It has also been claimed that if bright iron is immersed in water

practically free from oxygen and carbon dioxide, a minute amount of colloidal iron will form which will immediately oxidize if the water is allowed to come in contact with air.

Rust commonly met with in steel structures consists chiefly of iron combined with oxygen and water, forming a ferric hydrate, and has usually the familiar reddish brown color, but the true color is often disguised by the presence of deposited dust and traces of paint.

The product of corrosion is bulky, porous and hygroscopic. These properties tend to accelerate rusting, as the corroding influences in the form of vapors or liquids are attracted by and readily pass through the existing layer. Moreover, iron rust is electro-negative to iron, and furnishes innumerable local Voltaic couples in the presence of an electrolyte, which accelerate corrosion. Here, again, it will be observed that the hygroscopic nature of the rust constitutes a favorable channel for the electrolytic action. Upon removing apparently dry flakes of ferric oxide from a structure, a layer of moisture is often found between them and the steel. Thus, it can be understood that when rusting has once commenced it will readily proceed. Doctor Andrews showed that 50 per cent. more rust was deposited the second year compared with the first. It is unfortunate that the oxide, which forms on the surface of steel or iron assists in the process of rusting while the oxide coatings of other less commonly used metals such as aluminium, lead and copper, form a layer which protects the metal below.

It is recorded that some rejected plates from the Britannia Bridge, left unprotected upon a wooden platform exposed to the wash and spray of the sea, at the end of two years were so corroded that they could be swept away with a broom. They had an original thickness of seven-sixteenths to three-fourths of an inch. Basing calculation on the amount of corrosion which had taken place in the steel of the Britannia Bridge which had been kept well coated and clean, Baker found that it would take about 1200 years to corrode the plates entirely. Roughly, the plates, which are well looked after, will last 600 times as long as neglected plates. These facts are mentioned to show that so far as corrosion is concerned, the serviceable life of a structure or vessel can be extended enormously by careful attention to cleaning and recoating. H. L.

Crystal Structure of Complex Cyanides.—ROSCOE G. DICKINSON, of the California Institute of Technology (*Jour. Am. Chem. Soc.*, 1922, xliv, 774–784), has determined the crystal structure of certain complex or "double" cyanides by means of spectral photographs and unsymmetrical Lane photographs. The salts studied were potassium zinc cyanide, potassium cadmium cyanide, and potassium mercuric cyanide. These complex cyanides were found to have the same crystal structure as the minerals magnetite (ferrous ferrite, Fe_3O_4) and spinel (magnesium aluminate, $MgAl_2O_4$). J. S. H.

THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, May 17, 1922.*)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 17, 1922.

DR. WALTON CLARK, President of the Institute, *in the Chair.*

By consent the reading of the minutes of the previous meeting was dispensed with.

The Chairman announced that the annual presentation of The Franklin Medal, the Institute's highest award, in recognition of distinguished scientific and technical achievements, would be made and recognized Dr. Joseph S. Ames, Professor of Physics, the Johns Hopkins University, Baltimore, Maryland, who gave an account of the work of Sir Joseph John Thomson, Trinity College, Cambridge, England, recently awarded The Franklin Medal in recognition of "The immeasurable service he has rendered to the world as teacher and leader of thought in that domain of science, especially related to a fundamental knowledge of electricity and the constitution of matter."

Mr. R. L. Craigie, First Secretary of the British Embassy, Washington, District of Columbia, was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute, awarded to Sir Joseph John Thomson. Mr. Craigie conveyed the thanks of his government for the honors conferred upon his distinguished countryman.

Dr. Onward Bates was then recognized and described the work of Dr. Ralph Modjeski, of New York City, who had also been awarded The Franklin Medal in recognition of "His signal achievements as a designer and builder of structures, mainly bridges, many of them epoch-marking in the history of the engineering profession, beautiful as well as useful, involving on the part of the designer vision, courage and technic of the highest order."

Doctor Modjeski was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute. Doctor Modjeski expressed his thanks for the high honors conferred upon him.

The President then requested Mr. Coleman Sellers, Jr., Vice-president of the Institute, to take the Chair. Mr. Sellers recognized Mr. Nathan Hayward, who presented to the Institute, on behalf of its Board of Trustees, Board of Managers and Officers, a portrait of Dr. Walton Clark, painted by Mr. Lazar Raditz. Mr. Sellers accepted the portrait for the Institute.

The paper, "An Electron Theory of Solids," by Sir Joseph John Thomson, was read by Dr. Joseph S. Ames.

Doctor Modjeski then read his paper "Bridges—Old and New."

Adjourned.

R. B. OWENS,
Secretary.

(A full account of the meeting will appear in a later issue of the Journal.)

COMMITTEE ON SCIENCE AND THE ARTS.

(*Abstract of Proceedings of Stated Meeting held Wednesday, May 3, 1922.*)

HALL OF THE INSTITUTE,
PHILADELPHIA, May 3, 1922.

DR. JAMES BARNES *in the Chair.*

The following reports were presented for final action:

No. 2780: Rich System of Detecting and Extinguishing Marine Fires. The Certificate of Merit to Walter Kidde and Company, Incorporated, of New York.

No. 2786: Postage Meter. The Certificate of Merit to Mr. Arthur H. Pitney, of Stamford, Connecticut.

The following report was presented for first reading:

No. 2784: Oxidation of Benzene to Maleic Acid.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, April 6, 1922, with Dr. H. J. M. Creighton in the Chair. The minutes of the previous meeting were approved as read.

E. W. Washburn, Ph.D., of the Department of Ceramics of the University of Illinois delivered a lecture on "Physical Chemistry and Ceramics." The application of the methods of physical chemistry to the solution of various problems in the field of ceramics was described. The lecture was illustrated by lantern slides. The communication was discussed.

On motion of Prof. W. O. Sawtelle, a rising vote of thanks was extended to Doctor Washburn. The meeting then adjourned.

JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, April 13, 1922, at 8 o'clock, with Dr. Arthur W. Goodspeed in the Chair. The minutes of the previous meeting were approved as read.

K. T. Compton, Ph.D., Professor of Physics in Princeton University, Princeton, New Jersey, delivered a lecture on "The Physics of the Three-

Electrode Bulb." The Edison and thermionic effects were demonstrated; the properties of thermionic currents, the theories of thermionic emission, and the characteristics of evacuated and gas-filled bulbs were described. The lecture was illustrated by means of lantern slides and experiments.

The communication was discussed; a vote of thanks was extended to Doctor Compton, and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

Mechanical and Engineering Section.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, April 27th, at 8 o'clock, with Mr. A. W. Gibbs in the Chair.

The paper of the evening was presented by Dr. Frank J. Sprague, President of the Sprague Safety Control and Signal Corporation, New York City. The speaker described railroad operation of the United States which is mainly carried on under three methods of control—train orders, manual blocking and automatic block signals—the latter of which is the most modern and adds measurably to the safety and efficiency of operation. Despite these facts, up to the present is has been adopted on less than one-third of the trunk line mileage of the country.

This system is based upon the division of the tracks into blocks of various lengths, each fully or partly insulated from the other and supplied with current at its far end to normally energize a relay at the near end. These relays—active or not according as the blocks are occupied—control a system of motor-operated wayside signals inter-connected in such manner that they are made to show "danger," "caution" or "clear" indications, according to track conditions.

But these signals are after all but directional in character, and to be effective must be seen, understood and obeyed by the engineer. Experience has shown that these three essential conditions often are not met, from any one of many evident causes, and as a consequence disastrous end-on collisions not infrequently occur.

To overcome this defect in the present system of railroad operation many kinds of "automatic stops" and "automatic train controls" have been proposed, designed to protect the train in the event of failure of the engineer, but a satisfactory solution of the problem, that is, one which while affording ample protection will at the same time leave the engineer under all normal conditions in control of his train is a difficult one.

The present paper dealt with a specific development based upon the use of track magnets under control of the signal relay, to establish cab signals and to initiate the required braking, which system is being subjected to intensive tests on the New York Central Railroad. This system is based upon the same tract fundamentals as is the automatic signal system and can be used either independently of it, that is with cab signals only, or in connection with the wayside signals to combine them and the braking system of the train.

After a brief discussion a unanimous vote of thanks was extended to the speaker and the meeting adjourned.

ALFRED RIGLING,
Acting Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, May 10, 1922.)

RESIDENT MEMBERSHIP.

MR. SAMUEL SHOBER, Rittenhouse Club, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERSHIP.

MR. L. E. THOMAS, President, Reading Iron Company, Reading, Pennsylvania.

CHANGES OF ADDRESS.

MR. OLAF ANDERSEN, Norges Geologiske Undersokilse, Kronprinsensgt 2, Kristiania, Norway.
MR. FRANK M. ASHMEAD, The Locust, Atlantic City, New Jersey.
MR. D. B. HEILMAN, P. O. Box 453, Reading, Pennsylvania.
MR. JOHN W. HORNSEY, 2 Whitehall Court, London, S. W. 1, England.
MR. R. QUAYLE, 233 North Harvey Avenue, Oak Park, Illinois.
MR. J. STEPH. VAN DER LINGEN, Department of Applied Mathematics, University of Cape Town, Cape Town, South Africa.
MR. ETHAN VIALL, 7474 Lower River Road, Fernbank, Cincinnati, Ohio.

NECROLOGY.

Mr. Alfred Wolcott Gibbs, Wayne, Pennsylvania.

LIBRARY NOTES.

PURCHASES.

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BEST, WILLIAM N.—Burning Liquid Fuel. 1922.
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CROWTHER, J. A.—Ions, Electrons and Ionizing Radiations, Ed. 2. 1922.
Engineering Index for 1921. 1922.
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MANNING, H. P.—Fourth Dimension Simply Explained. 1921.
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RAYLEIGH, J. W. STRUTT, BARON.—Scientific Papers 1869–1919. 6 vols. 1899–1920.
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BOOK NOTICES.

ORGANIC CHEMISTRY, OR CHEMISTRY OF THE CARBON COMPOUNDS. By Victor von Richter. Edited by R. Anschütz and H. Meerwein, vol. ii, Chemistry of Carbocyclic Compounds. Translated from the Eleventh German Edition, by E. E. Fournier D'Albe, D.Sc., A.R.C.Sc. xvi-728 pages and index, 8vo. P. Blakiston's Son and Company, Philadelphia. Price $8.00 net.

Richter's chemistry in English form has been so long before the American public, and has been received with so much favor that but little opportunity is afforded to say anything new about it. The present translation is by a resident of England, and is certainly a work of immense detail and a thorough presentation of the multiplicities of combination of which the cyclic compounds are capable. The present edition embodies the same general character as the former ones, but is much extended and the mind is likely to become dazed by looking over the lists of derivatives from even the simplest of the molecules. The progress of this department of chemistry has brought out the structural formulas of many natural products, such as glucosides, colors and proteins which formerly were known only by their percentage composition, and for which purely arbitrary names had to be devised. Thus, the formula of amygdalin, the glucoside of many plants of the rose family, is given, showing it to be mandelo-nitrile diglucose.

The work maintains its standard as a very comprehensive enumeration of the data of organic chemistry. The present edition is well printed on good paper.

HENRY LEFFMANN.

THE CHEMISTRY OF THE NON-BENZENOID HYDROCARBONS AND THEIR SIMPLE DERIVATIVES. By Benjamin T. Brooks, Ph.D. 612 pages, including index, 8vo. The Chemical Catalog Company, New York, 1922. Price $7.00 net.

As Doctor Brooks remarks in the preface to this work, the attractive and facile chemistry of benzene and its related substances has diverted attention from other hydrocarbon groups. He suggests that this diverting affects unfavorably the compilation of text-books, in so far as the student is not given a proper picture of the close relationships and similarity of chemical behavior of the non-benzenoid groups. A reference is made to Wells' "Outline of History," but the reviewer is compelled to express a doubt whether that writer, though highly distinguished in general literature, is sufficiently acquainted with science to be able to give advice as to its methods or warn of its errors.

The book, of course, includes many cyclic compounds, large space being given to the terpene group. Doctor Brooks points out that while a large amount of work has been done in perfecting the engineering of petroleum, the urge in this direction has been mainly the profit derived therefrom, while a study of the purely chemical phases of the question has been comparatively neglected. Such studies will surely result in practical advantages, but after all, the research must be undertaken for the sake of ascertaining the truth whether such truth can be "made to pay" or not. "A great deal of painstaking systematic research in the field of the non-benzenoid hydrocarbons must be carried out, which may never be utilized in an industrial process." This sentence expresses the true purpose of science, which is the discovery of truth. The commercial value of the discovery must be regarded as merely incidental. In no phase

of chemistry is this fact better shown than in the work done in Germany in the study of the benzenoid groups, work largely carried out as pure science, but afterwards resulting in great industrial applications. It is, of course, true that after the initial discoveries had indicated valuable results, German chemists were principally directed to the practical lines, but at no time were the interests of pure science neglected. Many years ago, a German chemist said that it was due to the coöperation of theory and practice that the coal-tar industry of Germany had conquered the world, and, though at that time, many might have questioned the accuracy of the statement as to the conquest, the events of the war showed what had been accomplished.

Doctor Brooks emphasizes the need of intensive research in the field to which his book is devoted, pointing out the needs of petroleum, rubber, turpentine and essential oil industries for systematic theoretical information. American chemists have not been conspicuous in this line, as an enumeration of the leading authorities in it will show, for in such a list which is given, American names are noted by their absence. The book in hand is directed to presenting the ascertained data concerning the benzenoid hydrocarbons and to showing the close relationships which exist between many of them.

As an illustration of the value of theoretical discussion, the presentation of the theories of the double linking in the unsaturated olefines will serve well. The chemical behavior and physical properties of such molecules are fully as important as those of the true benzene type. Much attention is given in this chapter to the modifications of structure to which these ethylene groups are liable, and to the cyclic arrangements that they developed. That the group $>C=C<$ is unstable, or under stress, is indicated by a wealth of experimental evidence. The labors of Lewis and Langmuir in the study of atomic arrangements have been of value in explaining the theories of carbon linkings. The details of these applications are given considerable space, forty-six pages, elaborately illustrated by open chain and cyclic formulas, being devoted to the study of the "ethylene bond."

The book is divided into seventeen chapters, covering the field of the non-benzenoids and presenting in great detail the characters of the raw materials, the winning and nature of the crudes, preparation of the derivatives and properties thereof and the commercial and industrial relationships. An interesting series of data is that relating to the oxidation of the paraffines to fatty acids by direct oxidation, with or without the assistance of a catalyst. The shortage of fats in Germany during the war led to an active research as to the possibility of producing fatty acids from these hydrocarbons, in which a special commission was engaged under the direction of Engler. The data given out are, however, as is the case with much of the result of German war studies in chemical fields, somewhat scanty and contradictory, but it seems the best results have been obtained without a catalyst except a small amount of previously oxidized material as an initiator.

The descriptions are not limited to mere enumeration of the properties of the substances, but much space is given to supply and specific uses. Thus, the camphor outlook, both as to the natural and synthetic products, is given several pages, and in connection with petroleum the physical chemistry of lubricating oils is set forth.

The book is crowded with information on topics that are but scantily treated in ordinary text-books, and even in special works, and is a most valuable addition to the literature of hydrocarbon chemistry. The printing and illustrating (the latter principally structural formulas) are of the best quality, and the book is another one of those of recent appearance of which Americans may be proud, being one of the many indications that

"Westward the star of (chemical) empire takes its way."

HENRY LEFFMANN.

MESSUNG GROSSER GASMENGEN. Anleitung zur praktischen Ermittlung grosser Mengen von Gas-und Luftströmen in technischen Betrieben. By L. Litinsky, Chief Engineer, Leipzig. xv-266 pages, index, 138 illustrations, numerous tables, diagrams and a chart of comparative data concerning 18 methods of measurement, 8vo. Leipzig, Otto Spamer, 1922. Paper bound, 525 marks.

"Fuel economy is the slogan of the day." With this true and appropriate remark, the author of the book in hand begins his preface. With all classes of fuel, whether coal or oil as such, or the gaseous products therefrom, systems of economy are indispensable. An important step towards this is the correct measurement of the amounts used in industrial operations. The measurement of solid or liquid materials, horsepower, electric output may be regarded as solved problems, but gaseous fuels offer much greater difficulty. It is, however, a very important problem, and has been studied with great care. Much ingenuity has been shown in the construction of apparatus for measuring the large volume of gases employed or distributed by some of the great industries. The problems do not merely concern combustible gases; compressed air, sulphur dioxide, ammonia and chlorine are now prepared on the large scale, and an economy in regard to these is indirectly an economy of fuel, for, in the great majority of cases, industries have to consider the coal-pile. Progress in the application of exact measuring methods to gases has been somewhat retarded by the belief that they can be carried out only with great difficulty, whereas we are assured that there are now available simple and efficient apparatus for all purposes, apparatus that may replace the ordinary gas-meter, where that is not suitable. The great differences in the nature of gases render the problem, of course, more complicated than with solid or liquid materials. Gases respond so readily to differences of temperature and pressure, are so liable to contain impurities not evident to ordinary inspection, and possess such differences in their action on materials of construction, as witness the contrast between sulphur dioxide and ammonia, that many modifications must be made in the general type in order to adapt the apparatus to requirements of industries. The author has sifted the literature with great care, and has incorporated in the book an extensive bibliography, in which it is somewhat depressing to note the rarity of quotations from American sources. Whether this is due to the interruption of the opportunities to consult American books and journals during the past few years, or because the Americans have written but sparingly on the subject, cannot be determined here.

The author complains that in many establishments, even those recently equipped, no proper apparatus for gas measurement is installed. The work

is eminently practical; theoretical questions are not considered except in so far as they are necessary to a proper understanding of the methods. It is a pioneer work; the whole field of gas measurement is here presented for the first time.

An inspection of the book shows the extent and thoroughness of the author's labors, and exemplifies the inventive effort and genius that has been expended on this special field. No expense has been spared in the illustrations or tabular matter, and the printing and paper are of the best quality. Altogether the book is a standard treatise on a most important field of engineering, and author and publisher deserve the thanks of all who are occupied in the production or distribution of gaseous materials. The book will be a necessity for the gas-engineer's library.

HENRY LEFFMANN.

THE COAL INDUSTRY IN KENTUCKY. A Historical Sketch by Willard Rouse Jillson, B.S., M.S., D.Sc., Director and State Geologist of the Kentucky Geological Survey. 77 pages, index and plates, 12mo. Frankfort, Kentucky, The State Journal Company, 1922.

THE CONSERVATION OF NATURAL GAS IN KENTUCKY, the same author. 146 pages, index, plates, maps and diagrams, 12mo. Louisville, Kentucky, John P. Morton and Company, Incorporated, 1922.

In the first of the two books under consideration, Doctor Jillson has collected by diligent search in the archives of historical societies, a connected story of the development of the Kentucky coal-fields in its later phases, for it appears that the original find has not been recorded. Kentucky coal was used by the Aborigenes, not for fuel purposes, but for carving ornaments, cannel being especially used for this purpose. The author naturally expresses astonishment that the savages did not accidentally stumble upon the value of the material as fuel, especially as it is known that the southwestern Indians used coal for firing their pottery, and the records of the early white explorers of the region now included in Kentucky, show that outcrop coal was found in several places. Indeed, Doctor Jillson thinks that the Aborigenes must have used the material as fuel.

After discussing the history and early use, the present condition of the industry is set forth, and the volume closes with a chapter on the geology and production of coal. Fine grades of coal are mined in some parts of the state, especially cannel, the Kentucky fields containing the best grade of this species now mined in the United States. Much of this coal is shipped to the northwest and to Canada, being used for domestic purposes and for enriching illuminating gas. The work is illustrated with numerous photogravures, showing scenes in the mining regions.

The second volume discusses a subject of the greatest importance to the United States. As Doctor Jillson says, the problem of natural gas conservation is one requiring immediate action. He regards this as true especially in Kentucky, pointing out that the serious conditions that have arisen in adjoining states may be avoided in his own state if prompt action is taken. As in all movements for conservation, vested interests have to be combated, and the spirit that often actuates the owner of natural resources is that of Sir Boyle

Roche, who said in the Irish Parliament "Why do anything for posterity? What has posterity done for us?" Doctor Jillson, indeed, appropriately terms the present time "The Age of Waste." That many sources of raw materials are now approaching exhaustion is the opinion of those who have studied the subject, and natural gas is one that is perhaps nearest to this condition. In 1917 the peak production so far noted occurred, the output reaching over three-quarters of a billion cubic feet. Since then the production has been less and less each year. Oil reserves are also being seriously impoverished. The work in hand relates especially to the Kentucky natural gas supply and production, but the data are of value to all interested in the problem. The book is illustrated with a number of photogravures, representing actual conditions of avoidable waste in collection, transportation and distribution, and deserves wide circulation as a contribution to the cause of fuel economy. It is a neatly printed and well-written monograph.

HENRY LEFFMANN.

PENROSE'S ANNUAL. Volume 24 of the Process Year-Book and Review of the Graphic Arts. Edited by William Gamble, F.R.P.S., F.O.S. 64 pages, with many illustrations in color and plain, quarto form. Lund, Humphreys and Company, Limited, London, 1922. Price $4.00.

The merits of this book make it difficult for the reviewer to determine upon which to expend the most praise. It is a wonderful expression of high degree of excellence to which photography and its applications, engraving and printing have been carried. Illustrated with a great variety of plates and drawings, and containing much information as to the latest developments in photographic procedures, it takes place as the most valuable and interesting of our annuals. As might be expected, several firms are concerned in the production of the work, and their identity is set forth in detail, the paper from one source, the ink from another and so on. Among the most interesting novelties in procedure is the article by C. J. Killen on tests of acid restrainers for wet-plate development. The old iron-acetic mixture became somewhat scarce during the war on account of the official curtailment on the procuring of the acid. Mr. Killen found that nitric and sulphuric acids could be substituted without objection. He gives results with different proportions of these acids, the tests showing that both have a stronger preservative effect on the iron solution than acetic acid. The value of the method was amply demonstrated by practical trials in development, and for more than a year, nitric acid was used exclusively in the establishment.

A very vivid photogravure is that of the burial of the "unknown soldier" in Westminster Abbey. The book is agreeably free from the nudes, now so common in collections of photography, and by the irony of fate, the most striking group of this type, a photogravure of the "Three Fates" in the Gallery of Fine Arts at Brussels, is faced by the staid, spectacled portrait of the Principal of Saint Bride!

The opening chapter is a review of progress in process work, incidental to which a brief sketch is given of the advances made during the last quarter century. Allusion is made to death of Mr. Friese Greene, whose name is

connected with some of the most ingenious and important inventions in photography. He is generally credited by British writers as the initiator of motion picture methods, but French writers have recently grown quite irritated on this question, asserting strongly that practical procedures in this field are wholly due to men of their own country. It is difficult to decide the question, for as usual, the development of the motion picture industry has been the work of many minds, and it may be said that there is glory enough for all.

To the photographer, engraver and professional artist the book will be a valuable companion, and to the general public a revelation of what can be accomplished in the graphic arts.

HENRY LEFFMANN.

UNITED STATES LIFE TABLES, 1890, 1901, 1910 and 1901–1910. Prepared by James W. Glover, Expert Special Agent of the Bureau of Census. 476 pages and index, 4to. Government Printing Office, Washington, District of Columbia, 1921.

This extended and elaborated study of mortality statistics is one of benefits of the establishment of the census bureau as a permanent department of the government, instead of the older plan of gathering a miscellaneous set of officials every ten years. Mortality statistics are not matters of popular reading, but are of great importance in the study of hygiene and sociology. Unfortunately, the whole United States has not yet been brought under national control, and the collection of data is not carried out in a uniform manner. The present tables relate merely to mortality, and do not enter into the questions of the cause of death, upon which there may be much difference of opinion. It is stated in the preface that the figures show that from 1890 to 1910, mortality conditions have greatly improved for persons under 50, but have remained about stationary for those above that age. They also show great differences in the rates of mortality in different classes to the population, being much more favorable for women than for men, for persons residing in the country than for those in the city, for whites than for negroes, for native born than for foreign born. The favorable results for ages under 50 are probably largely due to the child-saving work of recent years. Interesting data are furnished as to mathematical methods of dealing with the figures and of the apparatus now applied for facilitating calculation.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 133. The Tail Plane. By Max M. Munk. 37 pages, illustrations, quarto. Washington, Committee, 1922.

This report deals with the calculation of the tail plane. The author has tried to simplify the present theory of longitudinal stability for that particular purpose so as to obtain one definite coefficient characteristic of the effect of the tail plane.

This coefficient is obtained by substituting certain aerodynamic characteristics and some dimensions of the airplane in a comparatively simple mathematical expression. Care has been taken to confine all aerodynamical information

necessary for the calculation of the coefficient to the well-known curves representing the qualities of the wing section. This is done by making use of the recent results of modern aerodynamics. All formulas and relations necessary for the calculation are contained in the paper. They give sometimes only an approximation of the real values. An example of calculation is added in order to illustrate the applications of the method.

The coefficient indicates not only whether the effect of the tail plane is great enough, but also whether it is not too great. It appears that the designer has to avoid a certain critical length of the fuselage, which inevitably gives rise to periodical oscillations of the airplane. The discussion also shows the way and in what direction to carry out experimental work.

Report No. 137, Point Drag and Total Drag of Navy Struts No. 1 Modified. By A. F. Zahm, R. H. Smith and G. C. Hill. 15 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

In this report are recorded the results of tests on struts conducted at the Washington Navy Yard. Two models of the modified Navy strut, No. 1, were tested in the 8 by 8 foot wind tunnel. The tests were made to determine the total resistance, and effect, and the pressure distribution at various wind tunnel speeds with the length of the strut transverse to the current. Only the measurements made at zero pitch and yaw are given in this report.

Report No. 140, Lift and Drag Effects of Wing-tip Rake. By A. F. Zahm, R. M. Bear and G. C. Hill. 9 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This pamphlet describes the tests carried out at the Washington Navy Yard on models of the RAF-6, Albatross, and Sloane aerofoils to determine the effectiveness of the conventional wing-tip rake in improving aerofoil characteristics. Two degrees of rake were tested on each model; the trailing edge being always longer than the leading edge. The results are compared with the values computed by standard formulæ in use at the time the tests were conducted.

Report No. 142, General Theory of Thin Wing Sections. By Max M. Munk. 19 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report deals with a new, simple method of calculating the air forces to which thin wings are subjected at small angles of attack, if their curvature is not too great. Two simple integrals are the result. They contain only the coördinates of the wing section. The first integral gives the angle of attack at which the lift of the wing is zero, the second integral gives the moment experienced by the wing when the angle is zero. The two constants thus obtained are sufficient to determine the lift and moment for any other angle of attack. This refers primarily to a two-dimensional flow in a non-viscous fluid. However, in combination with the theory of the aerodynamical induction, and with our empirical knowledge of the drag due to friction, the results are valuable for actual wings also. A particular result obtained is the calculation of the elevator effect.

PUBLICATIONS RECEIVED.

Penrose's Annual, volume xxiv of the Process Year-book and Review of the Graphic Arts. Edited by William Gamble, F.R.P.S., F.O.S., 1922. 91 pages, illustrations, colored plates, quarto. New York, Tennant and Ward, 1922. Price, $4.00.

The Chemistry of the Non-benzenoid Hydrocarbons and Their Simple Derivatives, by Benjamin T. Brooks, Ph.D. 612 pages, illustrations, 8vo. New York, The Chemical Catalog Company, 1922. Price, $7.00 net.

History of the Telephone and Telegraph in Brazil, 1851–1921, by Victor M. Berthold, Chief Foreign Statistician, American Telephone and Telegraph Company. 92 pages, 8vo. New York City, New York, 1922.

Chemische Technologie in Einzeldarstellungen, Herausgeber, Prof. Dr. A. Binz. Allgemeine Chemische Technologie. Messung grosser Gasmengen. Anleitung zur praktischen Ermittlung grosser Mengen von Gas—und Luftströmen in technischen Betrieben von L. Litinsky. 274 pages, illustrations, plates, 8vo. Leipzig, Otto Spamer, 1922. Price, paper, 525 marks.

Department of Commerce, Bureau of the Census: United States Life Tables 1890, 1901, 1910, and 1901–1910. Explanatory text, mathematical theory, computations, graphs, and original statistics, also tables of United States life annuities, life tables of foreign countries, mortality tables of life insurance companies. Prepared by James W. Glover, expert special agent of the Bureau of the Census. 496 pages, illustrations, diagrams, quarto. Washington, Government Printing Office, 1921.

Engineers' Club of Philadelphia: Report of the Sesqui-Centennial Committee on Sites. To the President and the Executive Committee of the Sesqui-Centennial Exhibition Association. 42 pages, plates, maps, oblong 8vo. Philadelphia, 1922.

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CURRENT TOPICS.

The Camphor Outlook.—The recently published work of Brooks on the "Non-benzenoid Hydrocarbons" devotes considerable space to the camphor problem, in relation to the practicability of the synthetic product competing with the natural. The large tree, *Cinnamomum camphora*, is the only source of the natural article and the process of distilling with steam the chipped wood of mature trees has been carried out in China and Japan for several centuries. Japan has acquired control of practically all of the region occupied by these trees, and the price of camphor has been deliberately advanced, which gave occasion to earnest efforts to produce it artificially. The greatly increased use of camphor, owing to the development of the manufacture of celluloid, still further much increased by the demand for photographic film, has added to the importance of this supply, as has also the demand for transparent windows for automobiles.

For the production of synthetic camphor, the successful methods employ turpentine or pinene as raw material, and unfortunately while the primeval camphor forests of Asia are being rapidly reduced, the American turpentine trees are also disappearing. Doctor Brooks expresses the hope that the substitution of light petroleum products in the paint and varnish industries will conserve much of the supply of turpentine. Efforts have been made to cultivate camphor trees, but the substance does not exude from the tree as does turpentine. The woody material must be distilled with steam. The distillation of leaves has not proved profitable. Considerable planting of camphor as trees has been done in Florida and California, as well as in some parts of the East Indies. Synthetic camphor is prepared from turpentine by conversion into bornyl chloride, the principal source of which is the long-leaved pine, *P. palustris*. The turpentine should be fresh, as old turpentine gives a low yield of bornyl chloride. Borneol, from which bornyl chloride is prepared, exists in Borneo camphor, but the supply from this source is not sufficient.

In this connection, however, a timely suggestion for increasing the yield of turpentine is presented in a paper by W. H. Mason, Laurel, Mississippi, which was read before the Southern Pine Association, and abstracted in *Building* (Philadelphia). Mason has carried out on a large scale, and with much success, two processes for extracting turpentine, pine oil and rosin from sawed lumber. In one process the drying is conducted mainly as in the ordinary dry-kiln method, but in the first 24 hours steam is used instead of air, and the vapors are led to a condenser. The condensed liquid consists of water and turpentine, which are separated. It is found that the lumber is dried better and more thoroughly, with less warping and will hold paint better. The process has been in use for more than a year.

The yield on long leaf pine is about one gallon of turpentine per 1000 feet; on short leaf pine about half this.

In the second method called "pitch extraction," only the pitch is treated. A grading expert marks the "fat" pieces, which are run into a special retort with steam coils in the bottom. Turpentine is run in and boiled up by which the pitch is extracted and water driven out. The solvent liquor is sent to the refining plant to recover the constituents. H. L.

The Adsorption of Gas Under Pressure. H. BRIGGS and W. COOPER. (*Proc. Royal Soc.*, Edinburgh, Vol. xli, Part II.)—Adsorbing material, such as charcoal, silica or coal, was dried and then used to fill a small steel cylinder. Dry gas was then compressed into the cylinder. The gas was later allowed to flow out through a meter, readings of pressure being taken from time to time. The cylinder was kept in a water-bath.

Activated cocoanut charcoal exhibited the greatest adsorption under pressure. A litre filled with this substance will hold at a pressure of 20 atmospheres 50 litres of nitrogen measured at normal pressure and at 15° C., or 36 litres of hydrogen, whereas in the absence of the charcoal it would hold only 20 litres of either gas on the supposition that Boyle's Law holds. "The gas-capacity of a cylinder intended to hold nitrogen under compression may be increased by filling the cylinder with dry cocoanut charcoal. The advantage gained by the charcoal is especially marked for pressures below 50 atmospheres. When blown off from 35 atmospheres, abs. to 1 atmosphere abs., for example, a cylinder containing cocoanut charcoal would discharge 66 per cent. more nitrogen than the same cylinder containing no adsorbent. Put in another way, the results indicate that a cylinder of 1 cubic foot water capacity filled with dry cocoanut charcoal and charged with nitrogen at 21 atmospheres would hold a total volume of 50 cubic feet of gas, of which 43.5 cubic feet would be discharged on the pressure being released to atmospheric. Had the cylinder not held charcoal it would require to have been charged to 44.5 atmospheres abs. to yield the same volume."

In several cases examined there is no such advantage obtained by the use of an adsorbent, but coal associated with outbursts of firedamp acted in the same way as the charcoal above. "By taking some anthracite ejected at an outburst in South Wales, drying it, and filling it into a gas-cylinder, and pumping in pit firedamp, it was found that one cubic foot of the coal was able to take up at 6 to 8 atmospheres pressure, and hold in a condition ready for almost instantaneous release, a quantity of firedamp considerably greater than could be contained in one cubic foot of open space charged with gas at the same pressure. The sudden outburst of gas constitutes, in fact, a problem in gaseous adsorption; the gas is held in the coal in a state available for discharge when the pressure is released."

G. F. S.

Pasteur Centennial.—Commemoration of the centennial anniversary of the birth of Pasteur will be the occasion of the erection of a statue facing the Strasbourg University, where as a professor, he began his career. The inauguration ceremonies will take place on May 1, 1923, under the patronage of the Republic, and will consist principally in the unveiling of the statue and the opening of an exhibition of Hygiene and Bacteriology. This exhibition will be mainly arranged to show the advances made in these subjects as a result of Pasteur's work. A Congress of Hygiene and Bacteriology will be held at the same time.

In estimating the work of Pasteur, his earlier investigations into the phenomena of racemism must not be forgotten. His later work in the study of pathogenetic organisms has overshadowed to a certain extent his labors in physical science, but these were epoch-making. His investigations extended over many years, the results appearing from time to time in French journals, with more or less extended abstracts in the journals of other countries, but in the early part of 1860 he delivered, by request, before the Paris Chemical Society, two lectures in which he summarized his labors, and set forth the interesting and highly important method of "mesotomization," that is, breaking up the racemic association so as to secure one of the active constituents. He also called attention to the curious asymmetry of the crystals of some of these compounds. His experiments were conducted on the tartrates. The two lectures have been printed in English as No. 14 of the "Alembic Club Reprints," with the title, "Researches on the Molecular Asymmetry of Natural Organic Products." A translation into German has appeared as No. 28 of Ostwald's "Klassiker der exacten Wissenschaften."

It is to be hoped that the orators to whom will fall the lot to deliver the addresses on the occasion of the dedication of the statue will not fail to lay some stress on the service which these early researches rendered to organic chemistry. H. L.

The American Philosophical Society, at its annual meeting on April 22nd, awarded the Magellanic Premium, established in 1786 by a friend of Benamin Franklin, to Paul R. Heyl and Lyman J. Briggs, conjointly, for the invention of the Earth Inductor Compass. It will be recalled that Doctor Heyl was the recipient some years ago of a part of the Boyden Premium from The Franklin Institute, for his investigation of the light from Algol with a view to solving the question raised by the donor "whether all rays of light, and other physical rays are or are not transmitted with the same velocity."

The close of the war left the air pilot without a compass that would function well under the adverse conditions of high speed, great acceleration, and sharp turns of direction prevailing in the aeroplane. The Bureau of Standards, therefore, at the request of the U. S. Air Service undertook the very practical problem of devising an adequate compass. As a result the two medallists have produced a

compass that consists essentially of a dynamo whose field is the magnetic field of the earth. The armature, consisting of four teeth or spokes of iron wrapped with coils and rotating in a horizontal plane, is driven with an angular velocity of 20 revolutions per second by an anemometer at the top of the vertical axis. Two pairs of brushes carry off the two direct currents to an apparatus in which the position of an index needle is determined by the currents. The arrangement is such that this needle stands at zero provided the airplane is on its prescribed course. A deviation from the course causes a corresponding departure of the needle from zero.

There are four special features in the compass—

1. The null method of setting the course.

2. The employment of iron in the armature, in contradistinction to the usual practice in earth inductors. Silicon iron is used which, very fortunately, has a high permeability for fields as strong as that of the earth and also a small retentivity. The use of the iron renders a smaller inductor possible, thus compensating for the additional weight due to the iron. The whole apparatus was not to exceed 25 pounds in weight. The finished compass actually weighs almost exactly one-half of this specified amount.

3. Distant control of the indicating apparatus. The dynamo is mounted in the back part of the fuselage, where it is out of the way and where, furthermore, there is the least motion.

4. A special arrangement to keep the axis of the dynamo vertical. In fact the armature swings on a short, heavy, damped pendulum. After a sharp turn it returns to verticality in a short time and in a dead-beat manner. The compass has stood the practical test of repeated flights and works well in all cases except in a few very special "stunt" evolutions. G. F. S.

Blast-furnace Slag for Roads. (*U. S. Department of Agriculture, Press Service Sheet No. 199.*)—Blast-furnace slag as a material for concrete road construction is to be thoroughly studied by the Bureau of Public Roads. With the enormous demand for road-building material, officials say, economy demands the use of material close at hand wherever possible, and the Bureau is now conducting investigations of different materials with this in view.

Great quantities of slag are to be found at blast furnaces in various parts of the country. Samples from 32 plants have been collected and will be made into concrete and tested for resistance to wear, strength, water absorption, and general utility. These results will be compared with similar tests made on other materials.

In addition to the laboratory tests it is possible that the experiments will be followed by an inspection of a number of concrete roads built with slag as the coarse material. These roads will be selected in various parts of the country and the reports, together with the laboratory tests, will furnish information which can be fully relied upon.

Platinum Conditions.—The enormous advance in the price of this metal in late years has proved very embarrassing to chemists and to several industries. This advance has unfortunately contributed to additional difficulty because it has diverted the metal to a use for which it is really not adapted, namely, jewelry. There is no reason to doubt that the practice of setting precious stones in platinum has been adopted because of the high cost of the material, for it has a poor lustre and does not set off the stone as well as gold. George F. Kunz has recently reviewed the conditions of the platinum supply and uses, and some of the data that he sets forth are here noted, being taken from recent issues of the *Chemical News*. The industry is gradually emerging from the chaotic condition into which it was plunged by the war, and even the Russian sources are beginning to be active. A notable increase of production is also recorded in Colombia, the locality, by the way, in which the metal was first detected. The Colombia mines were actively exploited while the Russian mines were blocked, but American companies are now endeavoring to stabilize the South American sources. The price of the metal has fallen somewhat, though still very high. An increased demand for jewelry and dental work has arisen since the close of the war which tends to keep up the price. In 1920 the consumption of platinum in the United States was 141,041 troy ounces, of which 57 per cent. was taken by jewelers, 19 per cent. by electrical industries, 11 per cent. by dental industries, 10 per cent. by chemical operations, the remainder being distributed in minor lines.

Naturally active search has been made for new platinum deposits, but so far no great rewards have come. Kunz states that the outlook for some Alaska exploitations is rather encouraging. In Colombia, the principal deposits are in the Atrato and San Juan Rivers, but a third river is regarded as likely to yield a supply. The United States is about to pay Colombia a large sum as indemnity, and it is hoped that much of this will be used to develop some of the Colombia industries, especially the platinum deposits. Undoubtedly a marked fall in the cost of platinum will be a great advantage to chemists.

H. L.

Application of the Electron Theory of Chemistry to Solids. SIR J. J. THOMSON. (*Phil. Mag.*, April, 1922.)—"Each kind of atom has associated with it a definite number of electrons which form its outer layer when it is in the free state: it is by the rearrangement of these electrons that it is able to hold other atoms, whether of the same or different kinds, in chemical combination. When these atoms aggregate and form a solid there will be in each unit volume of the solid a definite number of these electrons, and the problem is to distribute the electrons so that they will form with the atoms a system in stable equilibrium. . . . We shall begin with the simplest case when the atoms are all of the same kind, *i.e.*, when the solid contains only one chemical element. We suppose that the electrons

are arranged as a series of cells which fill space and that each cell surrounds an atom; the number of cells is equal to the number of atoms. If the atom is monovalent the number of electrons is equal to the number of atoms, if divalent to twice that number, if trivalent to thrice that number and so on. This condition will determine the shape of the cell. If the cells have to be similar and equal and to fill up space without leaving gaps, they must be of a limited number of types. These are as follows: (1) Parallelepipeda, if the atoms are of the same kind these may be expected to be cubes; (2) hexagonal prisms; (3) rhombic dodecahedra; (4) cubo-octahedra."

Let one illustration suffice for the type of reasoning employed. Suppose space to be filled with cells of cubical form packed one against the other, and at each of the eight corners of each cube let there be an electron, and, in addition, let there be an electron at the middle of each of the twelve edges of the cube. First, we consider the corner electrons alone. At each corner eight cubes meet and one electron is there, one-eighth of an electron to the account of each cube. The same holds for each of the eight corners of each cube. To the cube's account we therefore reckon eight times one-eighth or one entire electron. Now for the edge electrons. Only four cubes come together at this edge, so the electron at the middle of this common edge is divided equally between the four cubes. The cube has twelve edges, so to its account from the edges there are twelve times one-fourth or three electrons. One electron from the corners and three from the middles of the edges make a total of four for each cube, a possible arrangement for a tetravalant element, which turns out to be less stable than another arrangement. "For most of the valencies more than one arrangement of the electrons is possible, indicating that for such elements there might be allotropic modifications with different crystalline forms." The author next examines on dynamic grounds the stability of certain of the possible configurations of the electrons. This leads to a calculation of the maximum frequency of the vibrations of the electrons and some very satisfactory agreements between the outcome of theory and the data of experiment are noted. Similar agreements are further found in the cases of the bulk modulus and of the dielectric constant.

This paper marks a notable advance toward the complete understanding of crystals. G. F. S.

Decomposition of Ammonium Nitrate.—Interest in this subject has been developed of late owing to the great explosion at Oppau, the cause of which has not been determined, or if determined by the German experts, has not been definitely published. Suggestions have been made that it was in part due to ammonium compounds. The formula of ammonium nitrate indicates that it may be an explosive if the proper initiative is applied. At a moderate temperature it decomposes almost wholly into water and nitrous oxide, a procedure that has been used for many years on a very large scale for the manu-

facture of the well-known anæsthetic. It has been noticed, however, that irregular reactions often take place, especially the formation of small amounts of nitric oxide, and for commercial purposes the gas is always carefully purified. H. L. Saunders (*Jour. Chem. Soc.*, April, 1922, 698) gives the results of careful studies of the decomposition of the salt, finding that over a range of from 210° to 260° C. the course of decomposition is unaltered, about 98 per cent. of the salt decomposing into nitrous oxide and water, but a small amount of free nitrogen is always present. At a temperature of 300° the decomposition occurs explosively, and large amounts of nitrogen are set free. The reactions under the explosive decomposition are quite different from those which occur at the lower temperatures (quiet decomposition), producing nitric oxide, nitrogen peroxide and nitrogen in the ratio 2:4:5. Chlorides, which are often present in commercial samples, influence very unfavorably the action, free chlorine being almost always found in the gas. The higher the initial temperature of decomposition, the lower the proportion of nitrous oxide. A certain amount of liquid is produced which always contains nitric acid, and also hydrochloric when chlorides are present in the salt used. Sulphates are without special influence, and small amounts of sodium nitrate—a not infrequent impurity of the commercial salt—do not influence the decomposition below 250°. H. L.

Note on a Possible Relationship between the Focal Length of Microscope Objectives, and the Number of Fringes Seen in Convergent Polarized Light. F. I. G. RAWLINS. (*Phil. Mag.*, April, 1922.)—Observations were made with crystals of quartz, tourmaline and mica, having approximate thicknesses of 5, 4 and 1 mm., respectively. Daylight was used with a red filter. In accordance with a statement made in Groth's Optical Properties of Crystals it was found that the focal length of the objectives used determines the number of fringes seen in convergent polarized light. In the case of quartz with an objective of focal length 32 mm. no fringes at all were observed; two made their appearance with an objective of 22 mm. Corresponding numbers are 4, 16 mm.; 8, 8 mm.; and 11, 4 mm. Similar results hold for the two other crystals. The mathematical relation which appears to govern is this: "The rate of decrease of the number of fringes with focal length is proportional to the reciprocal of the focal length itself." G. F. S.

Electrolytic Preparation of Lead Arsenate.—HERMAN V. TARTAR and GARY G. GRANT, of the University of Washington (*Jour. Ind. Eng. Chem.*, 1922, xiv, 311–313), have devised a method for the preparation of lead arsenates by means of the electric current. Lead electrodes are used. When the bath contains disodium arsenate, the product contains a large percentage of a basic lead arsenate, $Pb_5.OH.(AsO_4)_3.3H_2O$. When the bath contains arsenic acid, the product contains a large proportion of lead arsenate,

$PbHAsO_4$; this salt is widely used as an insecticide. The conditions most satisfactory for the electrolysis are: A current density between 1.25 and 1.875 amperes per square decimetre, a distance between the electrodes of from 2.5 to 5.0 centimetres, a bath containing from 1 to 2 per cent. of sodium chlorate as an electrolyte and approximately 0.05 per cent. arsenic acid. Lead arsenate forms as a precipitate during the electrolysis. If the precipitate be permitted to stand in contact with the bath solution for several days, the proportion of the salt $PbHAsO_4$ is increased. When several per cent. of arsenic acid are added to the bath, the precipitate does not form, and lead is deposited on the cathode. J. S. H.

Measurement of the Pressure of the Sun's Atmosphere. A. PEROT.. (*Comptes Rendus*, April 3, 1922.)—About a year ago Perot pointed out the possibility of measuring pressures within gaseous masses by studying the connection between the pressure and the ratio of the wave-lengths of two radiations either emitted or absorbed by the gas. These two radiations must be differently affected by pressure. This procedure is independent in its results of both the Doppler and of the Einstein effects. The application of this method by its author to that region of the sun's atmosphere where the *b* lines of magnesium are absorbed indicated that the pressure there is practically zero. Later Salet found pressures of some tenths of an atmosphere to obtain where the iron lines originate in the sun and in certain stars. Now Perot has used five iron lines, two of which have a high pressure coefficient and the others a low one. He obtains these values for the pressure in the sun 38, 24 and 41 cm. of mercury, agreeing well with Salet's results.

An interesting by-product of these results is that they remove some anomalies in certain comparisons made by Fabry and Buisson and thus indirectly strengthen Einstein's law. G. F. S.

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WALTON CLARK	FREDERICK ROSENGARTEN

*Deceased

MEETINGS

COMMITTEE ON SCIENCE AND THE ARTS. First Wednesday of each month, 8 P.M. (except July and August).

BOARD OF MANAGERS. Second Wednesday of each month, 3.30 P.M.

INSTITUTE. Third Wednesday of each month (except June, July, August and September), 8 P.M.

SECTION MEETINGS. Thursday Evenings (except week of Institute Meeting), 8 o'clock. October 1 to April 30.

CHANGES OF ADDRESS

Members are particularly requested to inform the Secretary of changes of address.

MEMBERSHIP.

Terms and Privileges.

THE MEMBERSHIP OF THE INSTITUTE is divided into the following classes, viz.: *Resident Members, Stockholders, Life Members, Permanent Members, Non-resident and Associate Members.*

Any one interested in the purposes and objects of The Institute and expressing a willingness to further the same may become a member when proposed by a member in good standing and elected by the Board of Managers.

TERMS.—Resident members pay Fifteen Dollars each year. The payment of Two Hundred Dollars in any one year secures Life Membership, with exemption from annual dues.

STOCK.—Second-class stockholders pay an annual tax of Twelve Dollars per share, and the holder of one share is entitled by such payment to the privileges of membership.

PRIVILEGES.—Each contributing member (including non-residents) and adult holder of second-class stock is entitled to participate in the meetings of The Institute, to use the Library and Reading Room, to vote at the Annual Election for officers, to receive tickets to the lectures for himself and friend, to attend the Section meetings and to receive one copy of the JOURNAL *free* of charge, except associate members, who may not take part in elections.

PERMANENT MEMBERS.—The Board of Managers may grant to any one who shall in any one year contribute to The Institute the sum of One Thousand Dollars a permanent membership, transferable by will or otherwise.

NON-RESIDENT MEMBERS.—Newly elected members residing permanently at a distance of twenty-five miles or more from Philadelphia may be enrolled as Non-resident Members, and are required to pay an entrance fee of Five Dollars, and Five Dollars annually. Non-resident Life Membership, $75.00.

Contributing members, if eligible, under the non-resident clause, on making requests therefor, may be transferred to the non-resident class by vote of the Board of Managers, and are required to pay Five Dollars annually.

ASSOCIATE MEMBERS.—Associate members are accorded all the privileges of The Institute, except the right to vote or hold office, upon the payment of annual dues of Five Dollars. This class of membership is limited to persons between the ages of seventeen and twenty-five years. Upon reaching the age limit they become eligible to the other classes of membership.

RESIGNATIONS *must be made in writing, and dues must be paid to the date of resignation.*

For further information and membership application blanks address the SECRETARY OF THE INSTITUTE.

AWARDS BY THE INSTITUTE

The following awards are made by The Franklin Institute:

The Franklin Medal (Gold Medal and Diploma).—This medal is awarded annually from the Franklin Medal Fund, founded January 1, 1914, by Samuel Insull, Esq., to those workers in physical science or technology, without regard to country, whose efforts, in the opinion of the Institute, acting through its Committee on Science and the Arts, have done most to advance a knowledge of physical science or its applications.

The Elliott Cresson Medal (Gold Medal and Diploma).—This medal is awarded for discovery or original research, adding to the sum of human knowledge, irrespective of commercial value; leading and practical utilizations of discovery; and invention, methods or products embodying substantial elements of leadership in their respective classes, or unusual skill or perfection in workmanship.

The Howard N. Potts Medal (Gold Medal and Diploma).—This medal is awarded for distinguished work in science or the arts; important development of previous basic discoveries; inventions or products of superior excellence or utilizing important principles; and for papers of first importance that have been published in its JOURNAL.

The Edward Longstreth Medal (Silver Medal and Diploma).—This medal is awarded for inventions of high order and for particularly meritorious improvements and developments in machines and mechanical processes. In the event of an accumulation of the fund for medals beyond the sum of one hundred dollars, it is competent for the Committee on Science and the Arts to offer from such surplus a money premium for some special work on any mechanical or scientific subject that is considered of sufficient importance.

The Certificate of Merit.—A Certificate of Merit is awarded to persons adjudged worthy thereof for meritorious inventions, discoveries or improvements in physical processes or devices and for papers of special merit that have been published in its JOURNAL.

The Boyden Premium.—Uriah A. Boyden, Esq., of Boston, Mass., has deposited with THE FRANKLIN INSTITUTE the sum of one thousand dollars, to be awarded as premium to "any resident of North America who shall determine by experiment whether all rays of light, and other physical rays are or are not transmitted with the same velocity."

For further information relating to these awards apply to the Secretary of the Institute.